

## Supplementary information

### Effects of substituents on the photophysical/photobiological properties of mono-substituted corroles

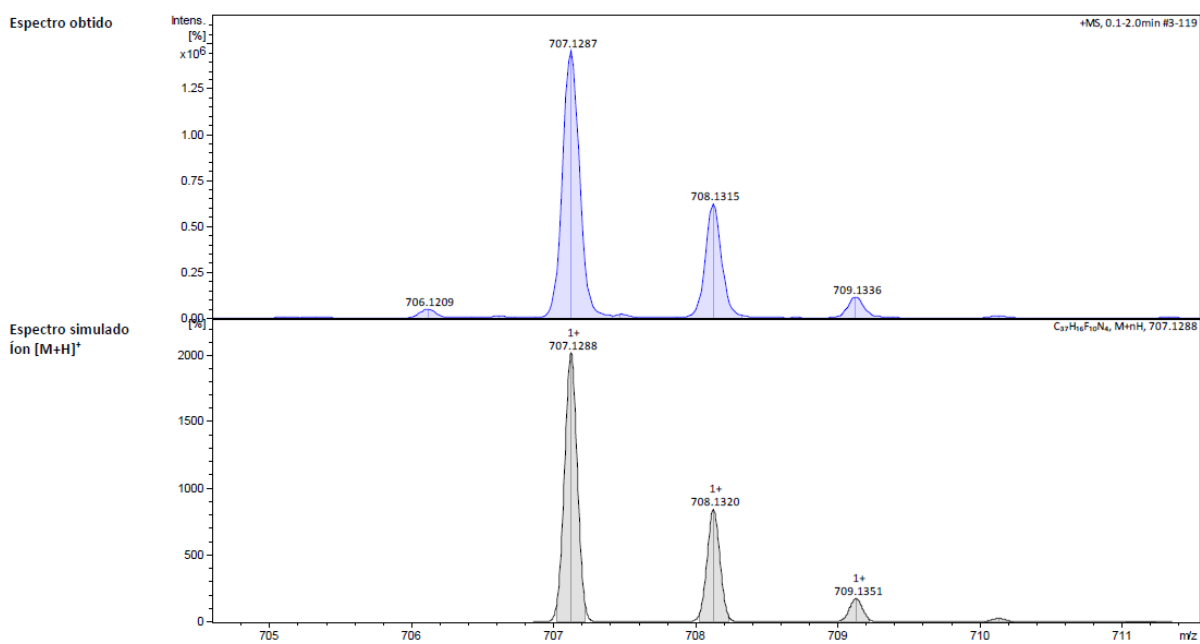
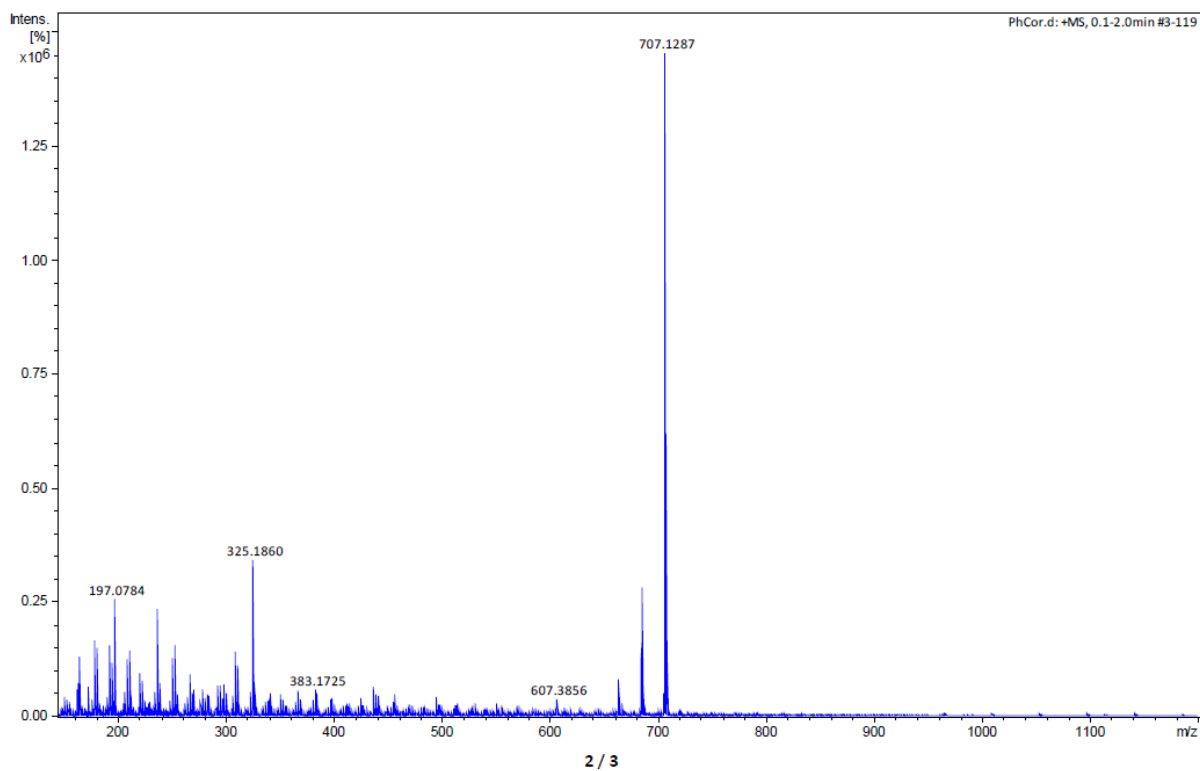
Vitória Barbosa de Souza<sup>1</sup>, Vinícius N. da Rocha<sup>2</sup>, Paulo Cesar Piquini<sup>2</sup>, Otávio Augusto Chaves<sup>3</sup> and Bernardo A. Iglesias<sup>1,\*</sup>

<sup>1</sup>*Department of Chemistry, Bioinorganic and Porphyrinoids Materials Lab, Federal University of Santa Maria, 97105-900, Santa Maria, RS, Brazil*

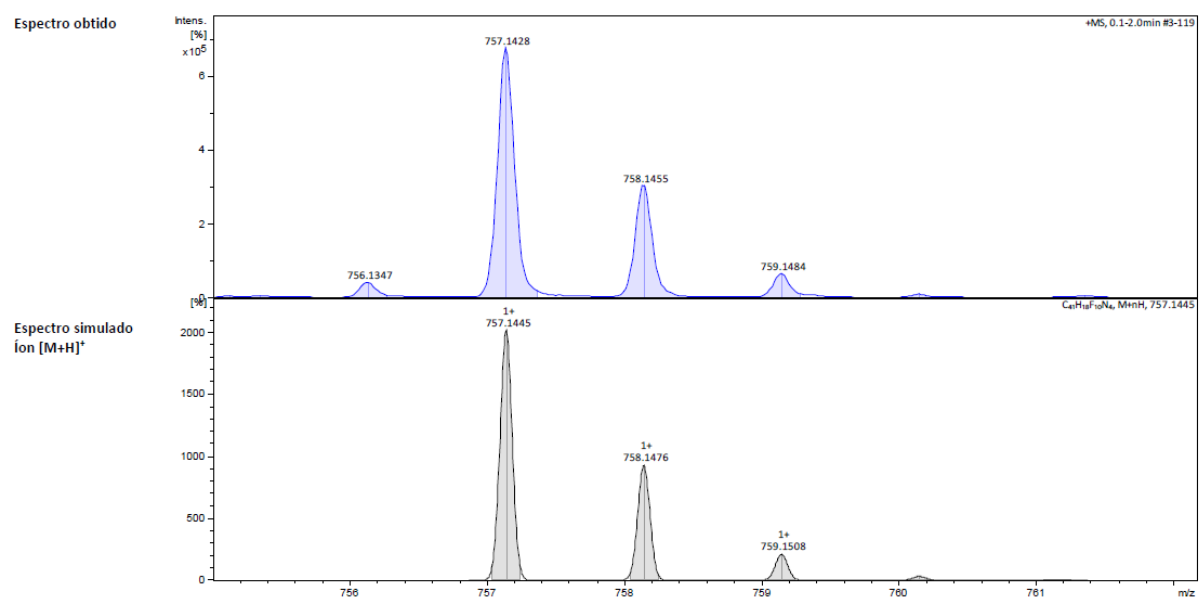
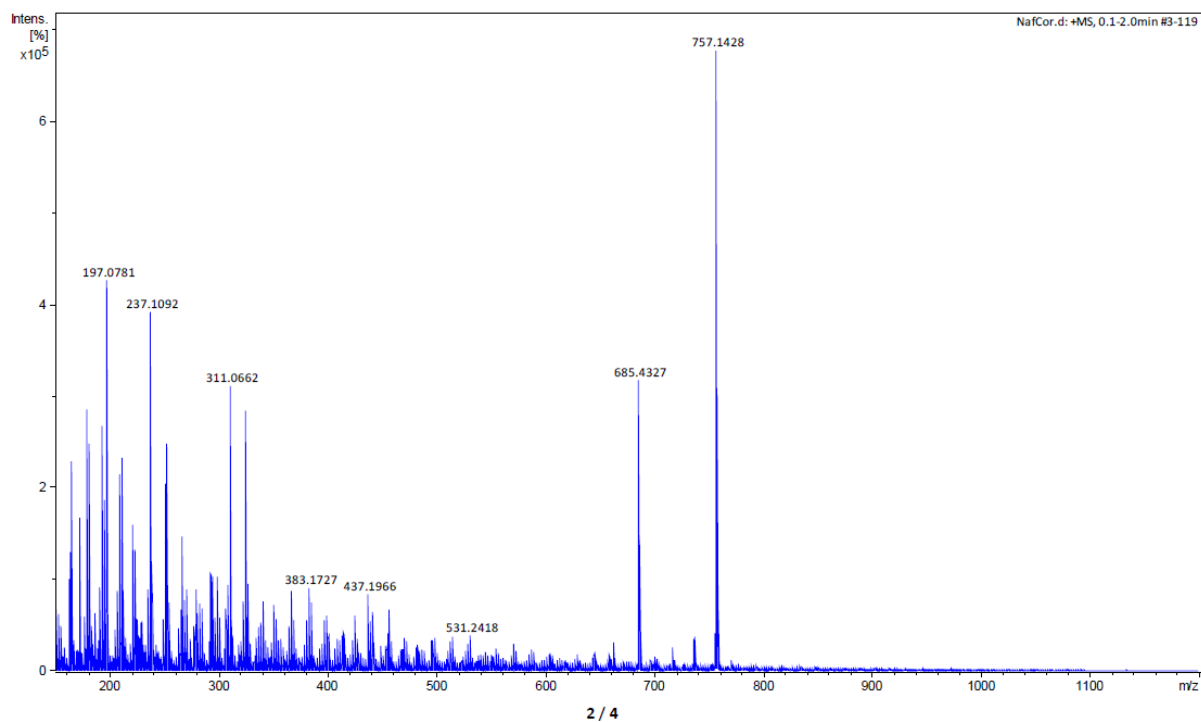
<sup>2</sup>*Department of Physics, Federal University of Santa Maria, 97105-900, Santa Maria, RS, Brazil*

<sup>3</sup>*CQC-IMS, Department of Chemistry, University of Coimbra, Rua Larga, 3004-535, Coimbra, Portugal*

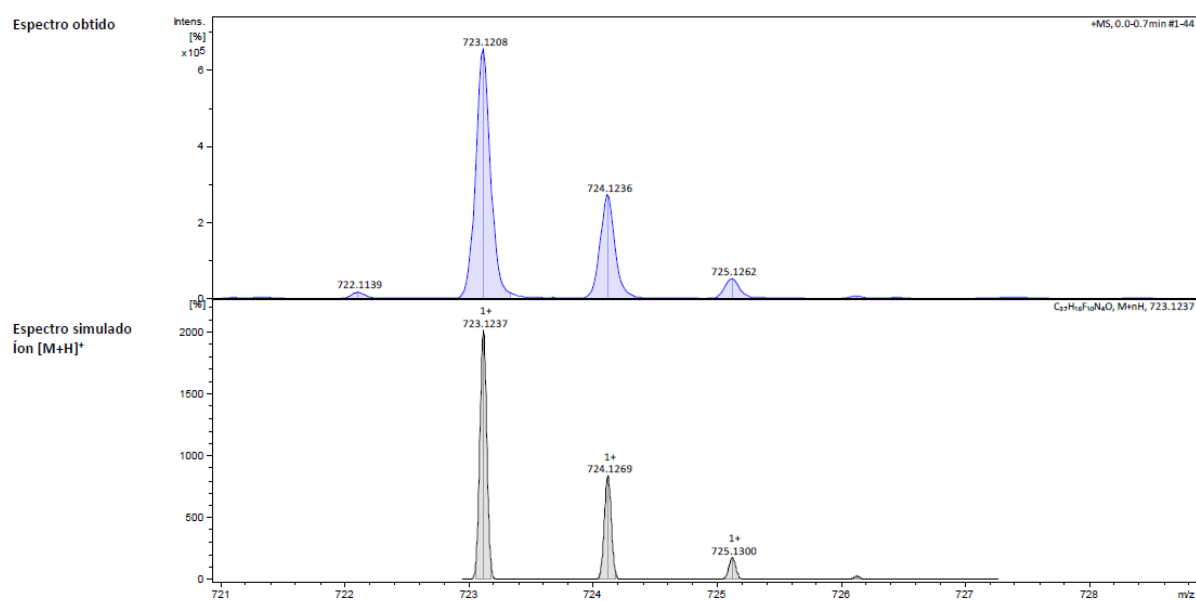
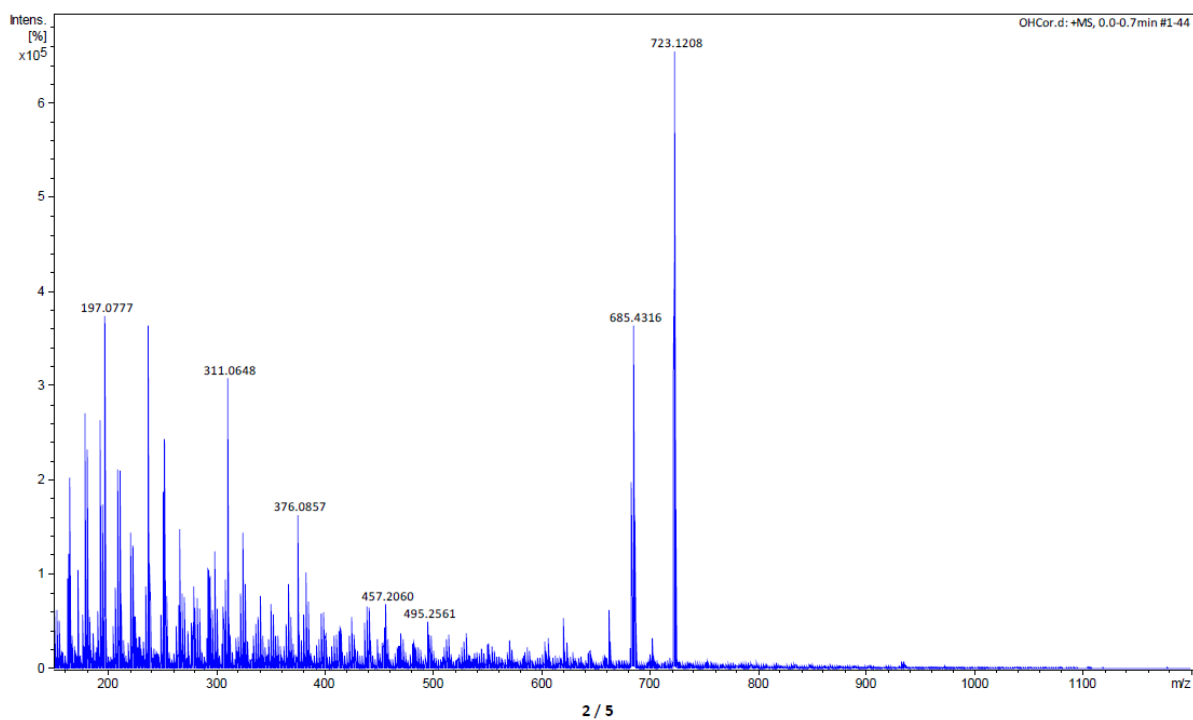
\*Correspondence: bernardopgq@gmail.com; bernardo.iglesias@ufsm.br (B.A.I.)



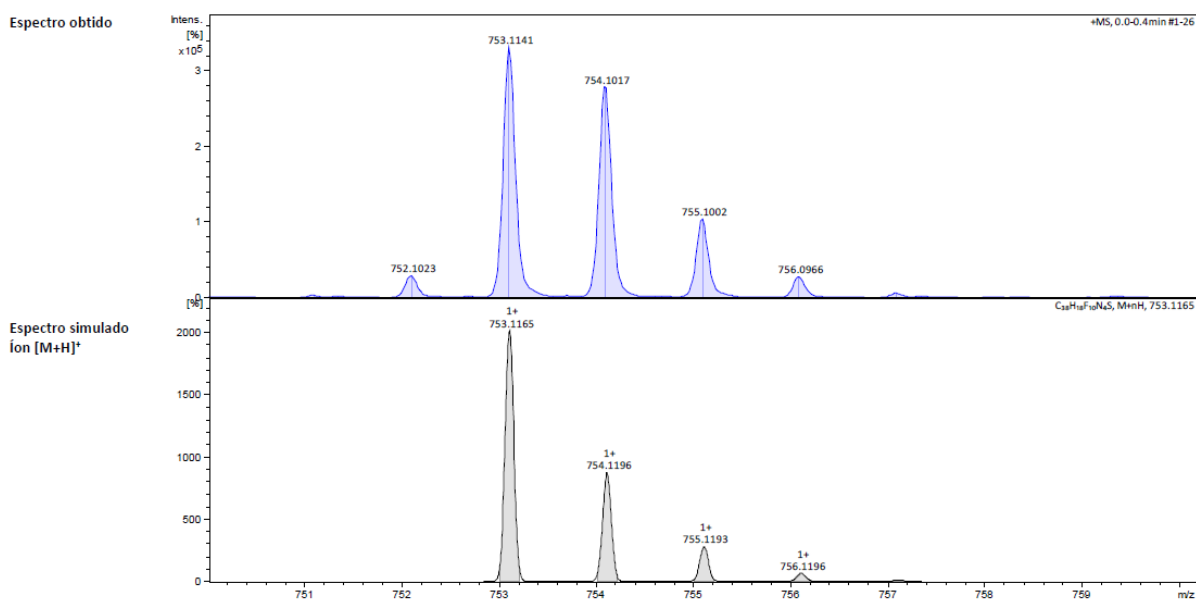
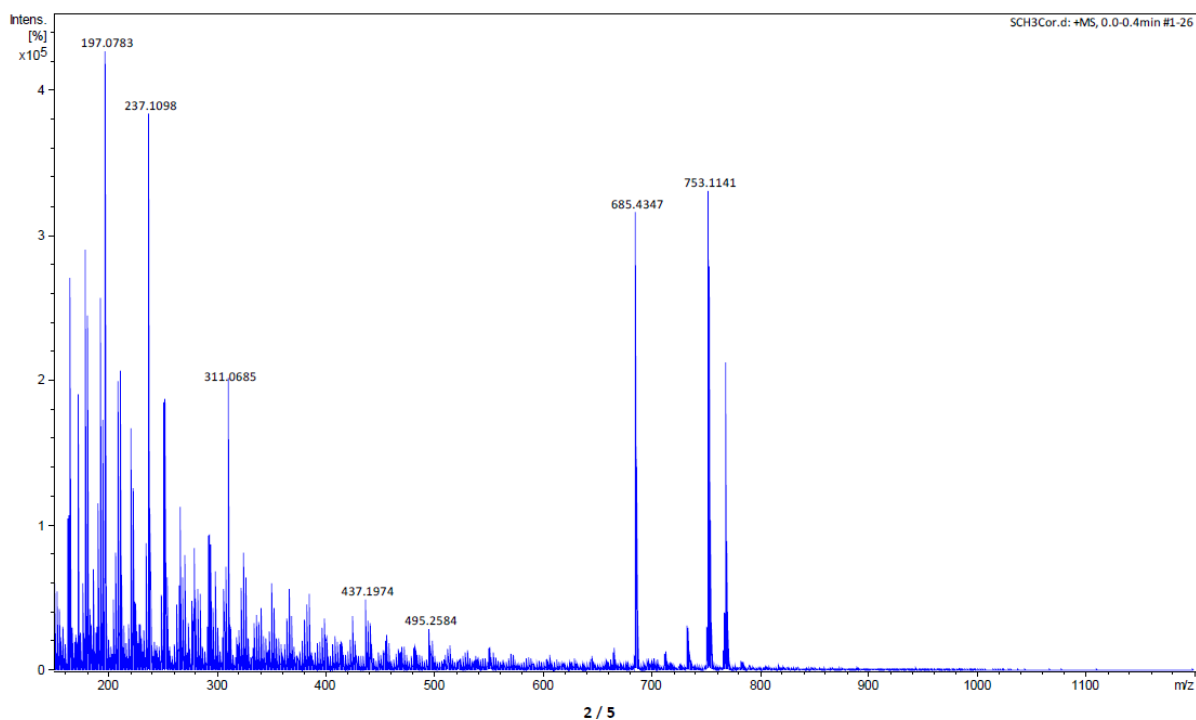
**Figure S1.** HRMS-ESI(+) mass spectrum of corrole **1**.



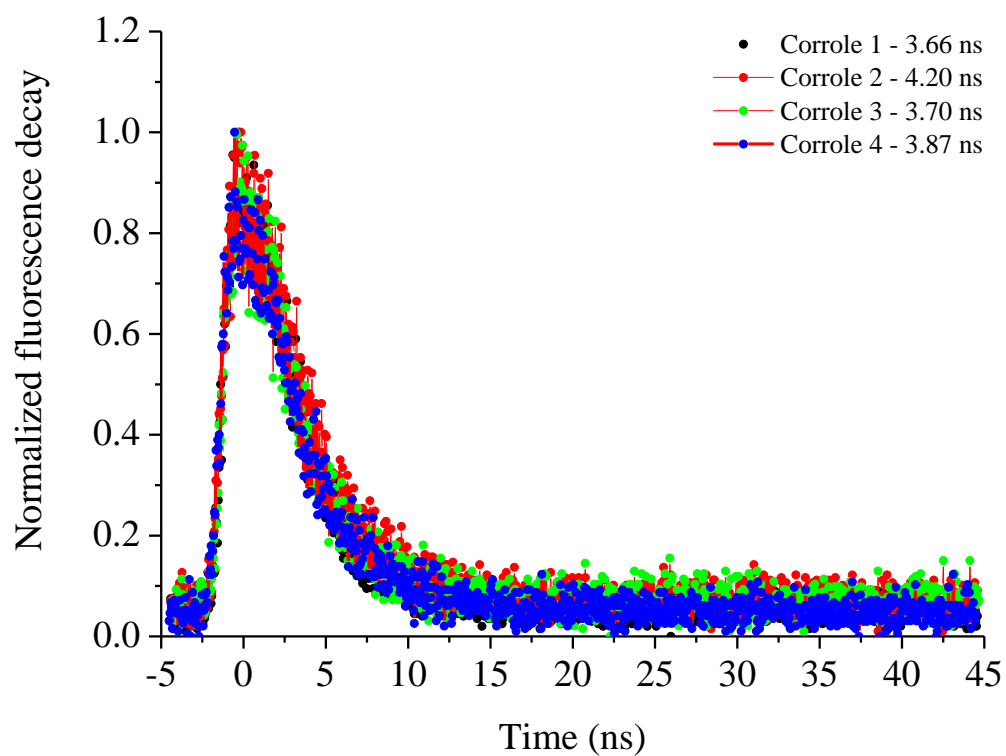
**Figure S2.** HRMS-ESI(+) mass spectrum of corrole **2**.



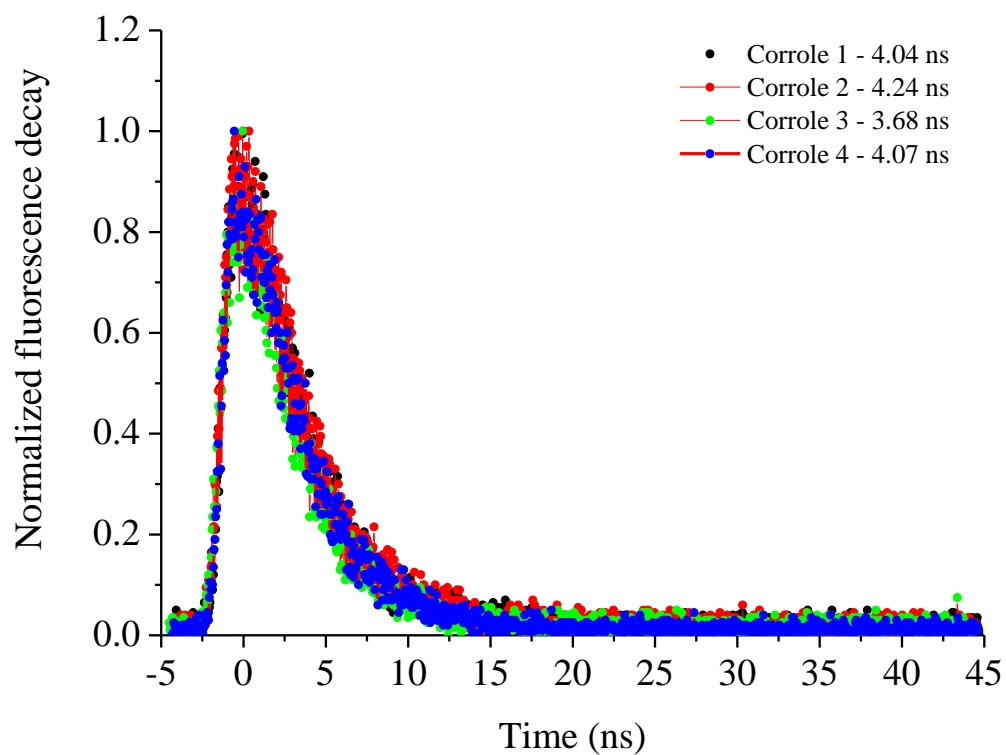
**Figure S3.** HRMS-ESI(+) mass spectrum of corrole 3.



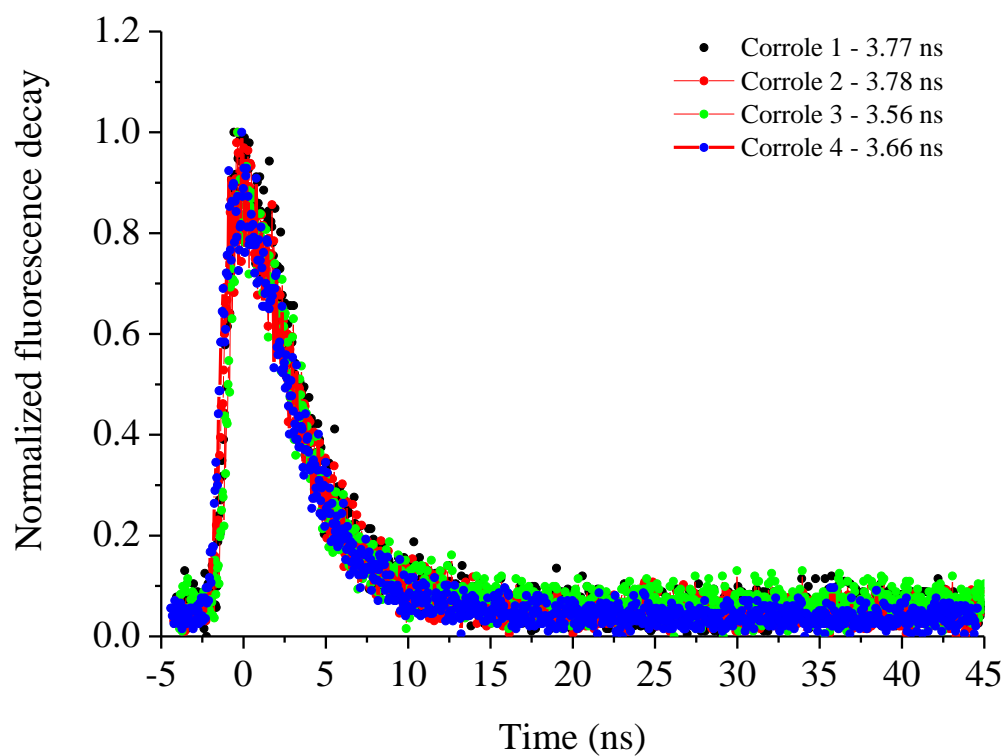
**Figure S4.** HRMS-ESI(+) mass spectrum of corrole **4**.



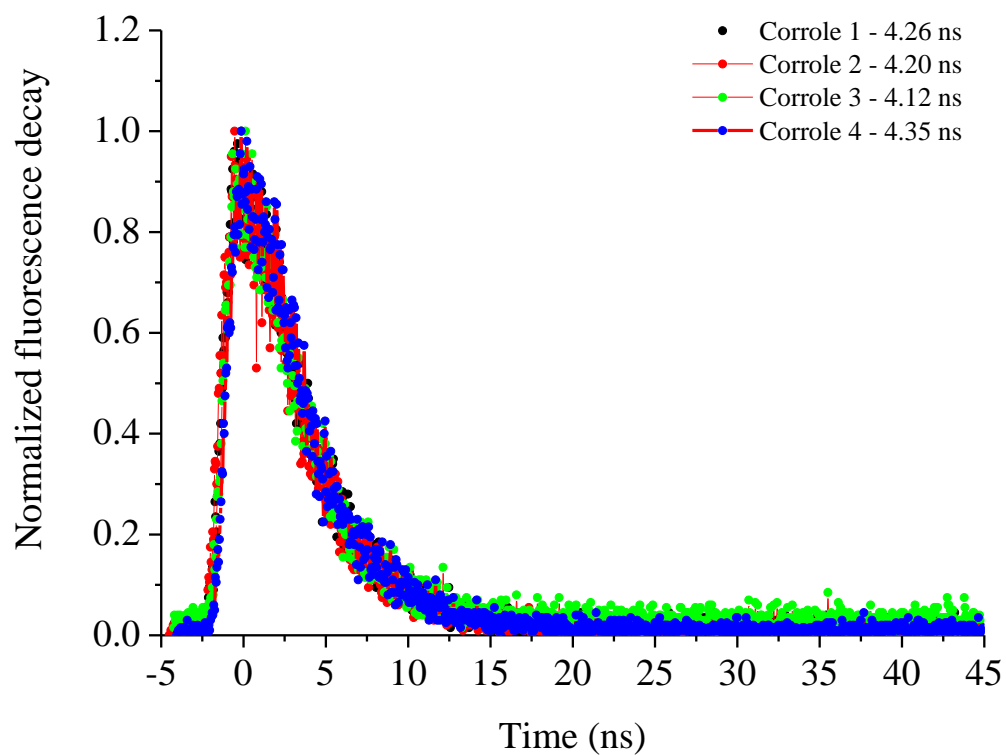
**Figure S5.** Normalized fluorescence decays of corroles **1-4** in DCM solution.



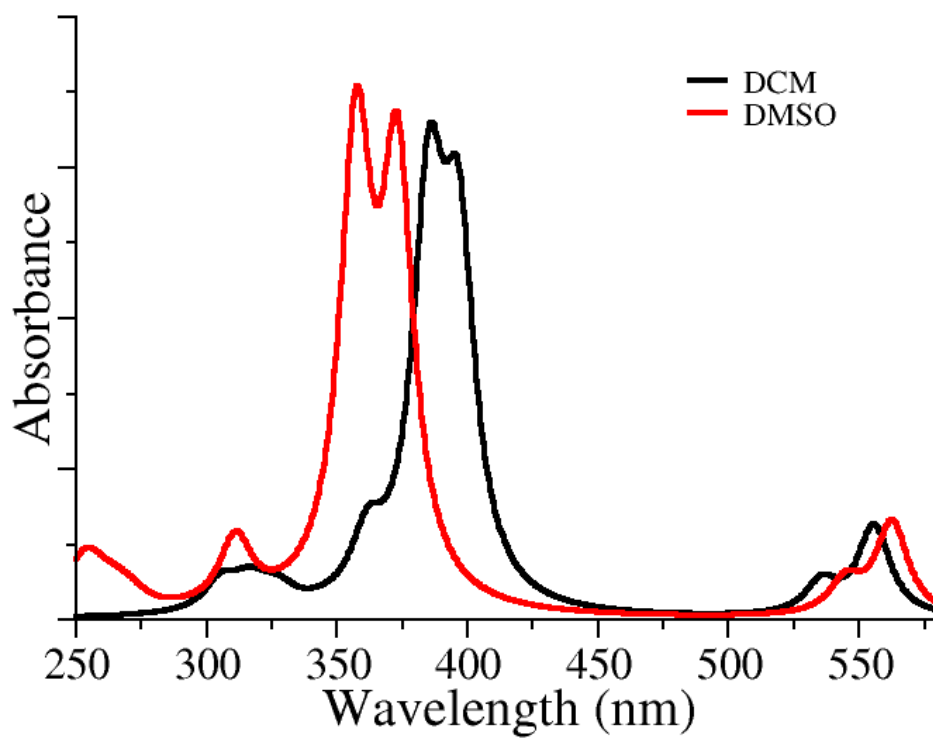
**Figure S6.** Normalized fluorescence decays of corroles **1-4** in ACN solution.



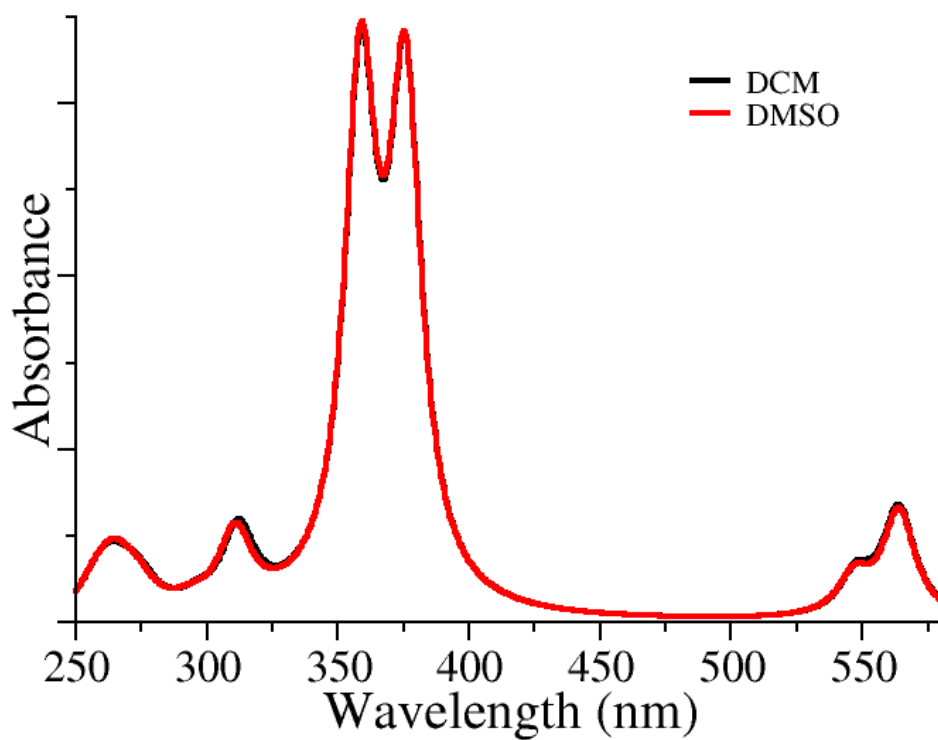
**Figure S7.** Normalized fluorescence decays of corroles **1-4** in MeOH solution.



**Figure S8.** Normalized fluorescence decays of corroles **1-4** in DMSO solution.

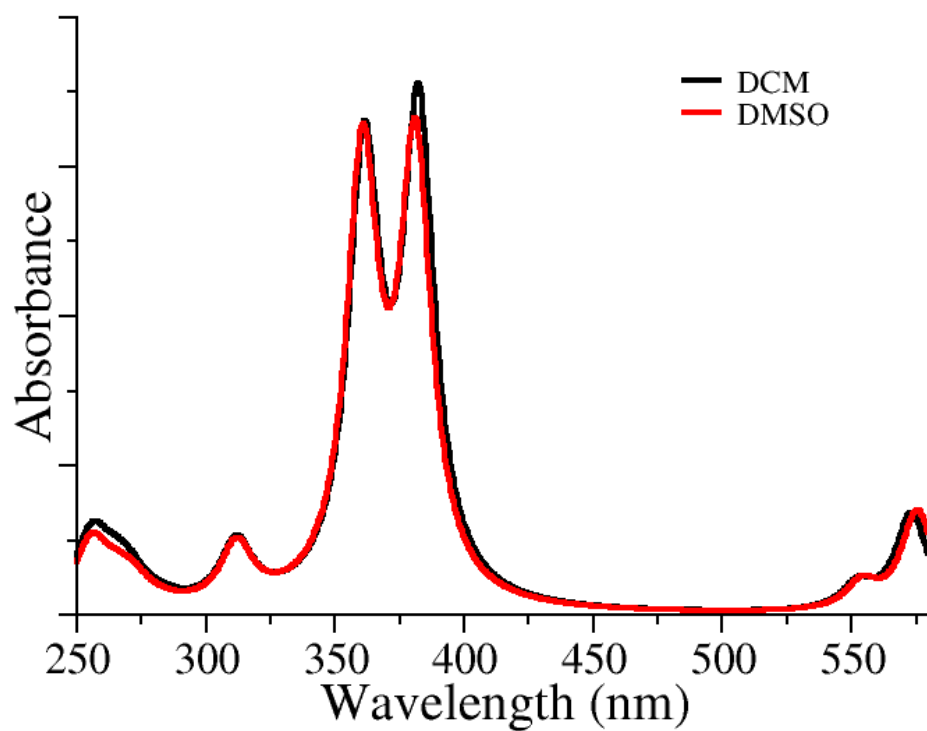


**Figure S9.** Theoretical optical absorption spectra in DCM and DMSO of corrole 1.

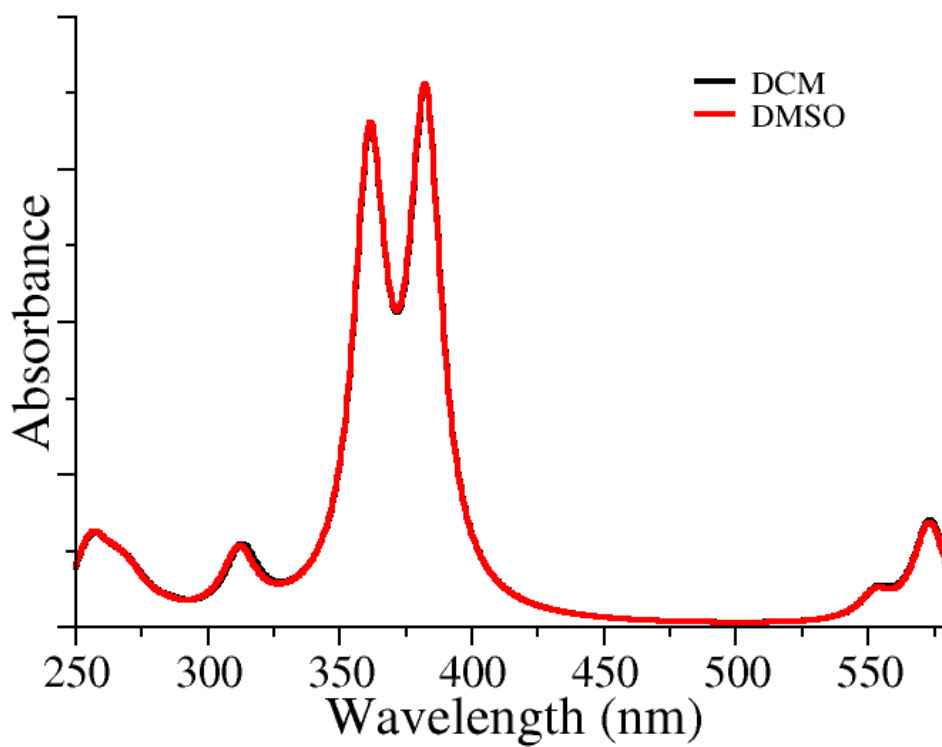


**Figure S10.** Theoretical optical absorption spectra in DCM and DMSO of corrole 2.

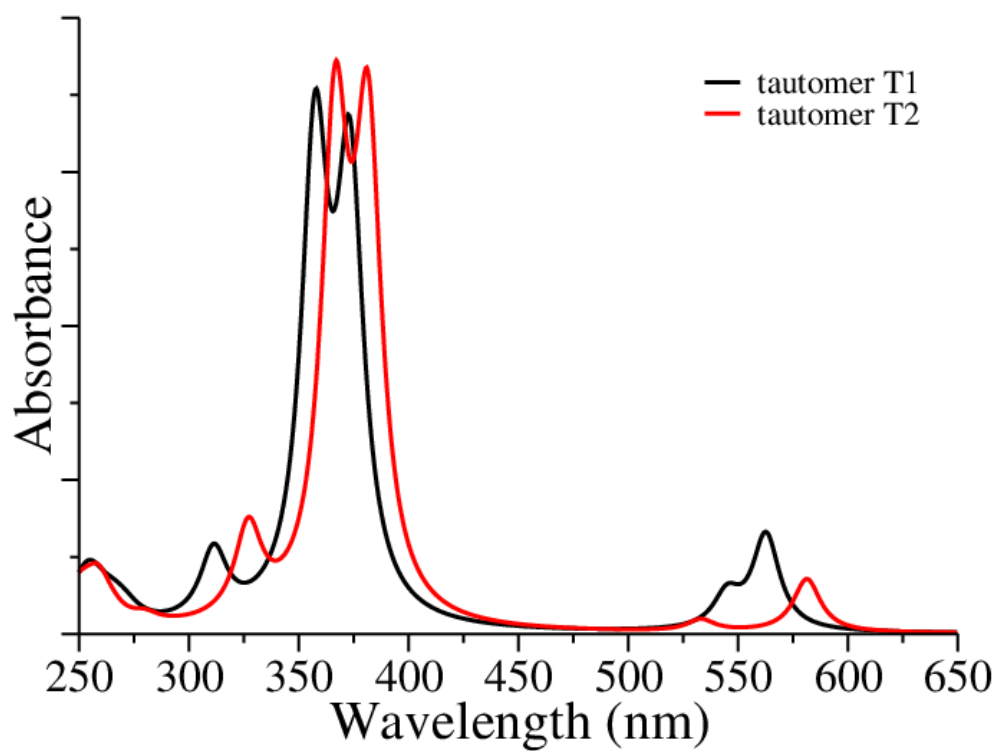




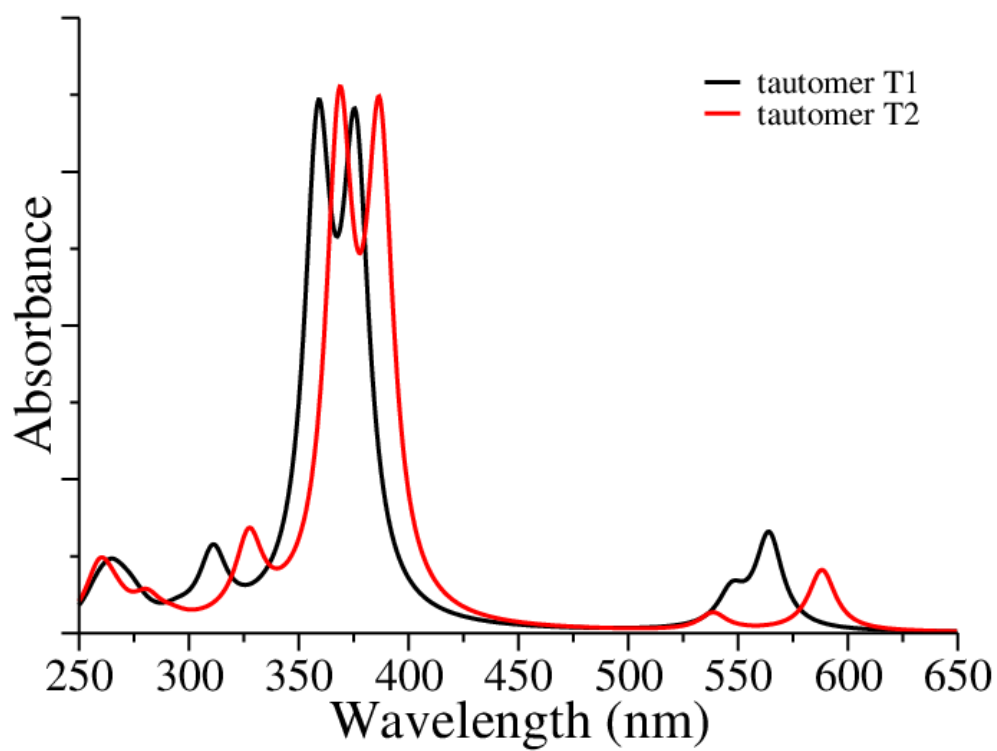
**Figure S11.** Theoretical optical absorption spectra in DCM and DMSO of corrole 3.



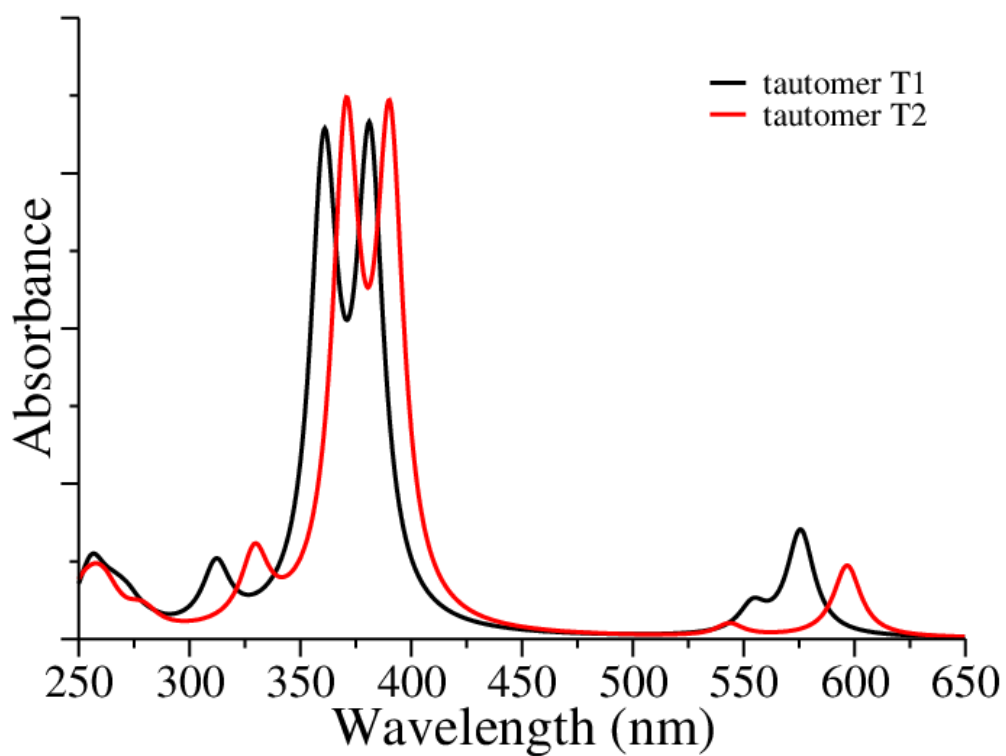
**Figure S12.** Theoretical optical absorption spectra in DCM and DMSO of corrole 4.



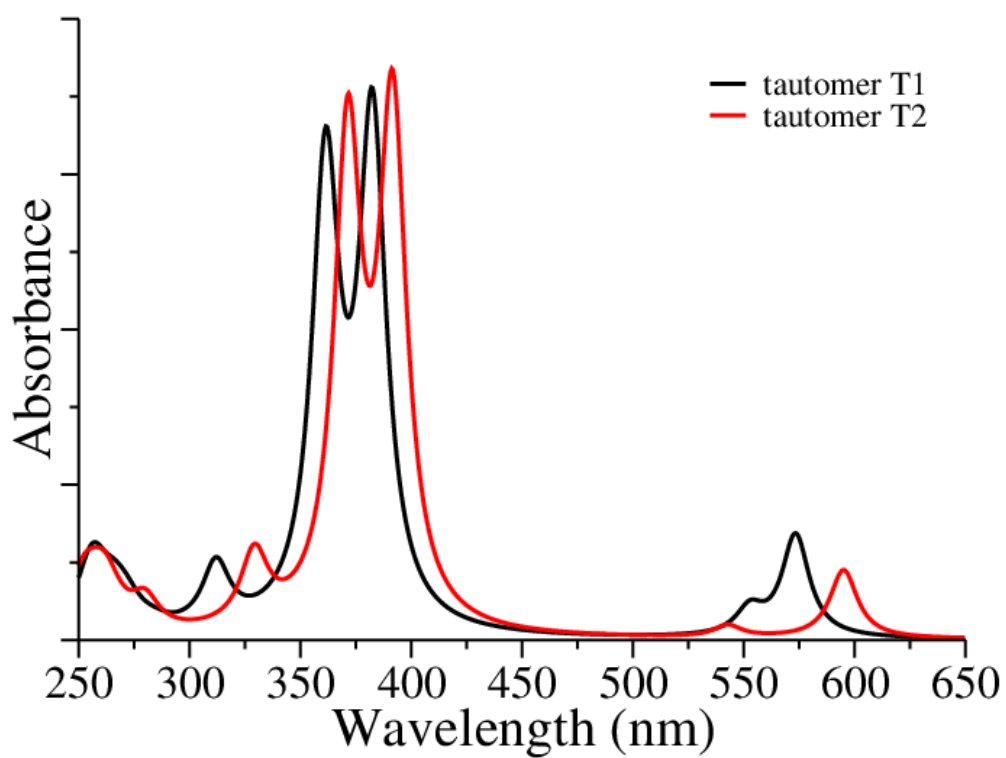
**Figure S13.** Theoretical optical absorption spectra in DMSO of tautomeric states of corrole 1.



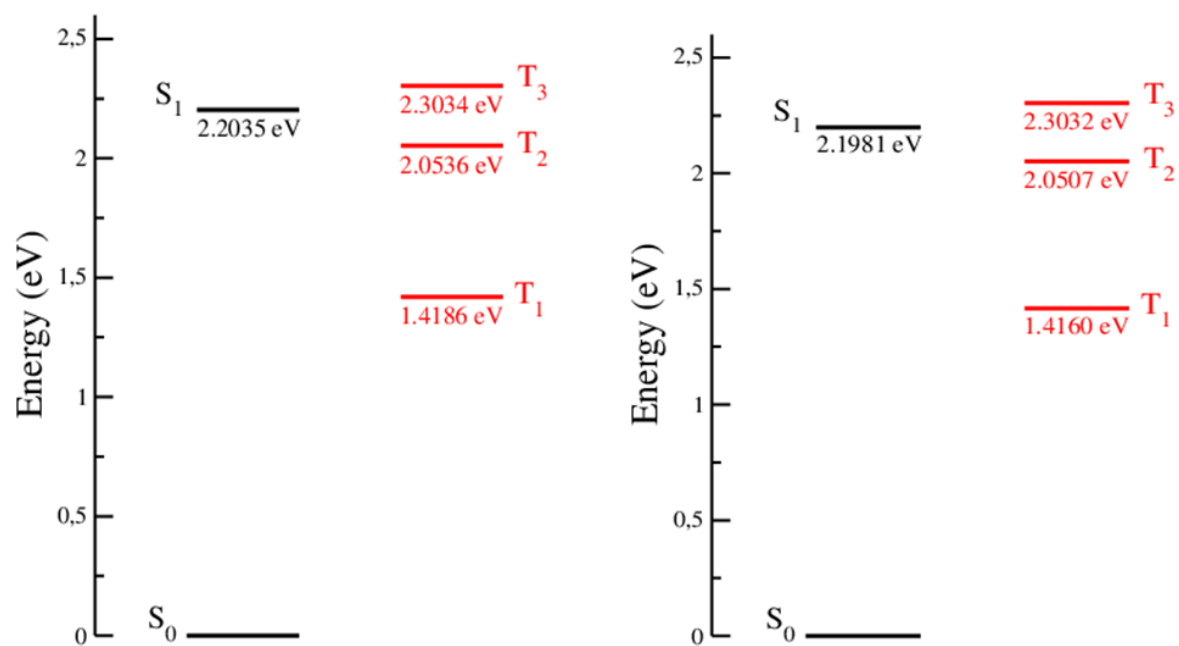
**Figure S14.** Theoretical optical absorption spectra in DMSO of tautomeric states of corrole 2.



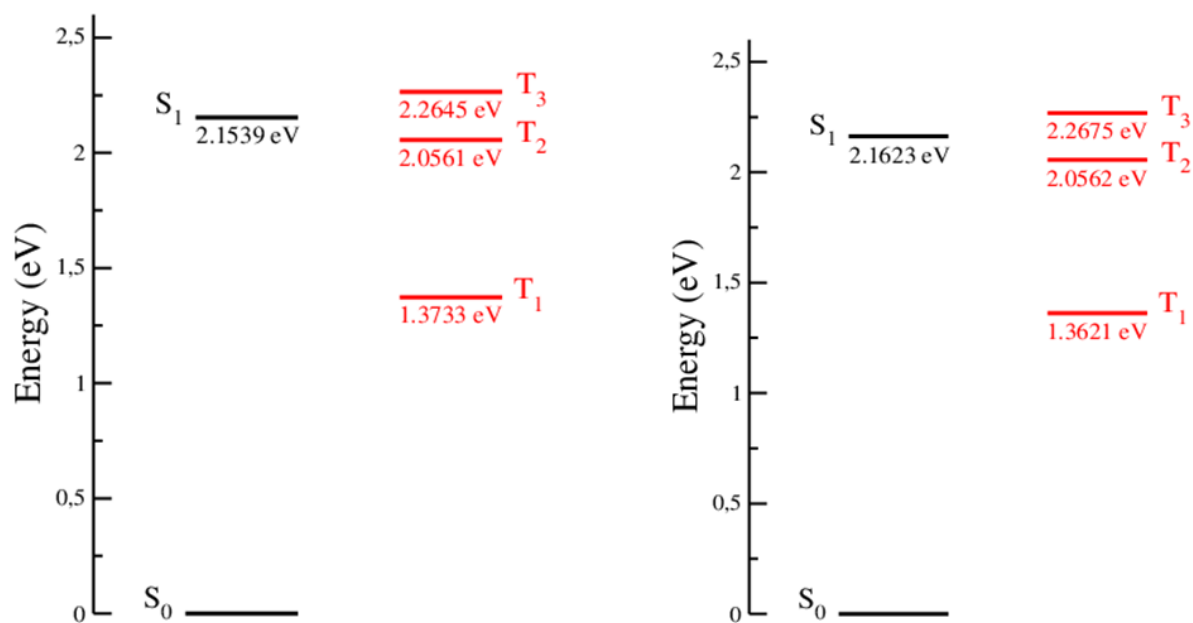
**Figure S15.** Theoretical optical absorption spectra in DMSO of tautomeric states of corrole **3**.



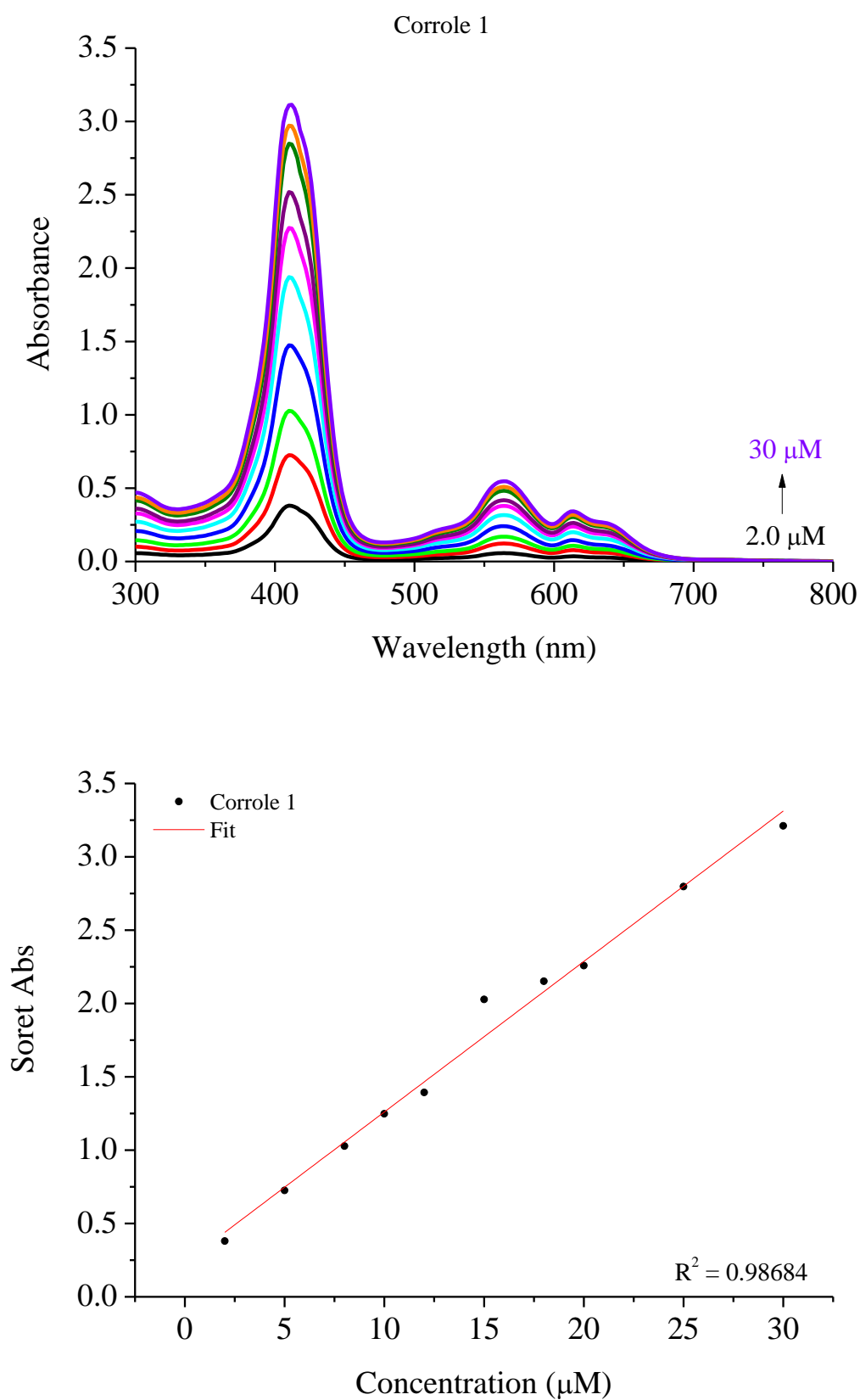
**Figure S16.** Theoretical optical absorption spectra in DMSO of tautomeric states of corrole **4**.



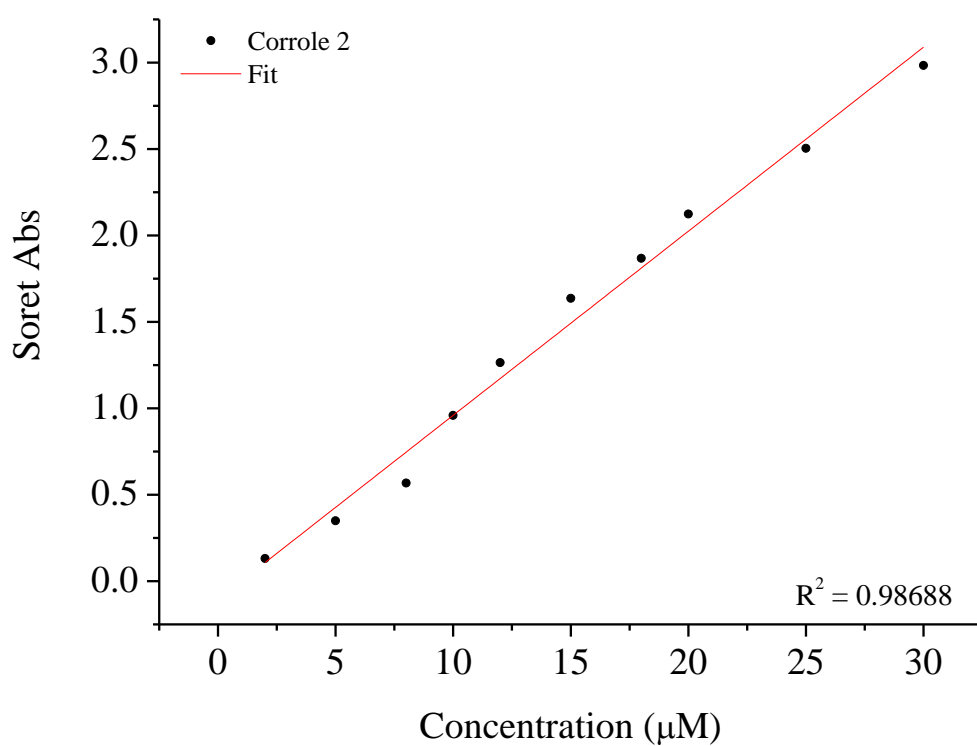
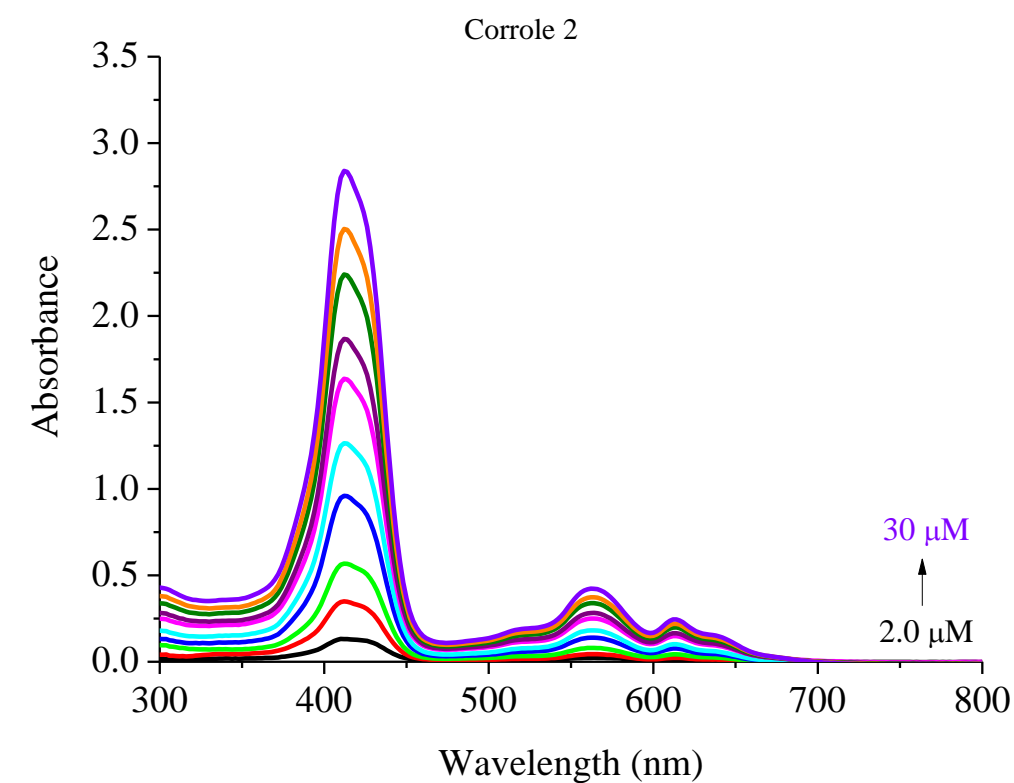
**Figure S17.** Total energies of the  $S_1$  and  $T_1$ ,  $T_2$  and  $T_3$  excited states, relative to the ground state  $S_0$  of corroles **1** (left panel), and **2** (right panel).



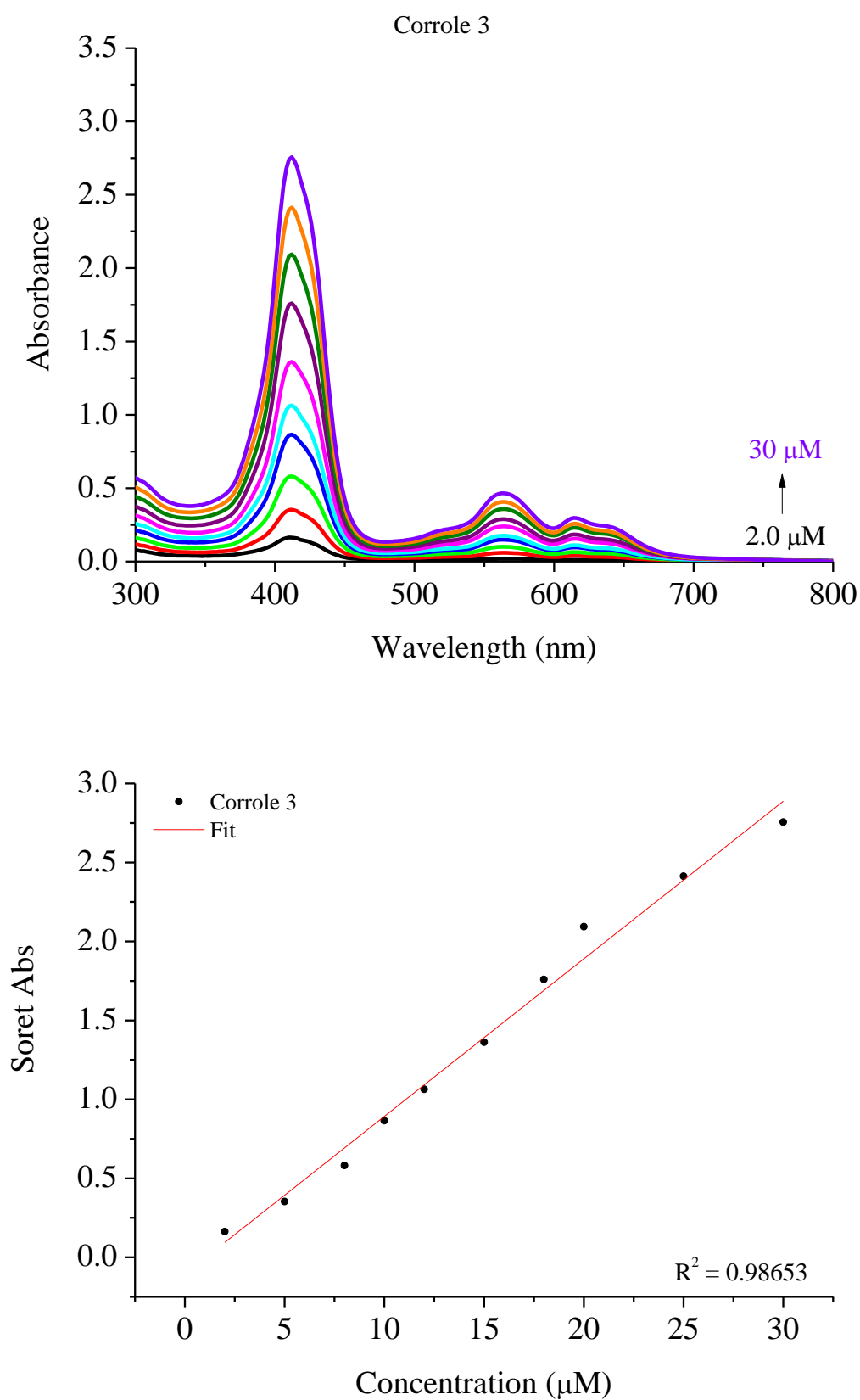
**Figure S18.** Total energies of the  $S_1$  and  $T_1$ ,  $T_2$  and  $T_3$  excited states, relative to the ground state  $S_0$  of corroles **3** (left panel), and **4** (right panel).



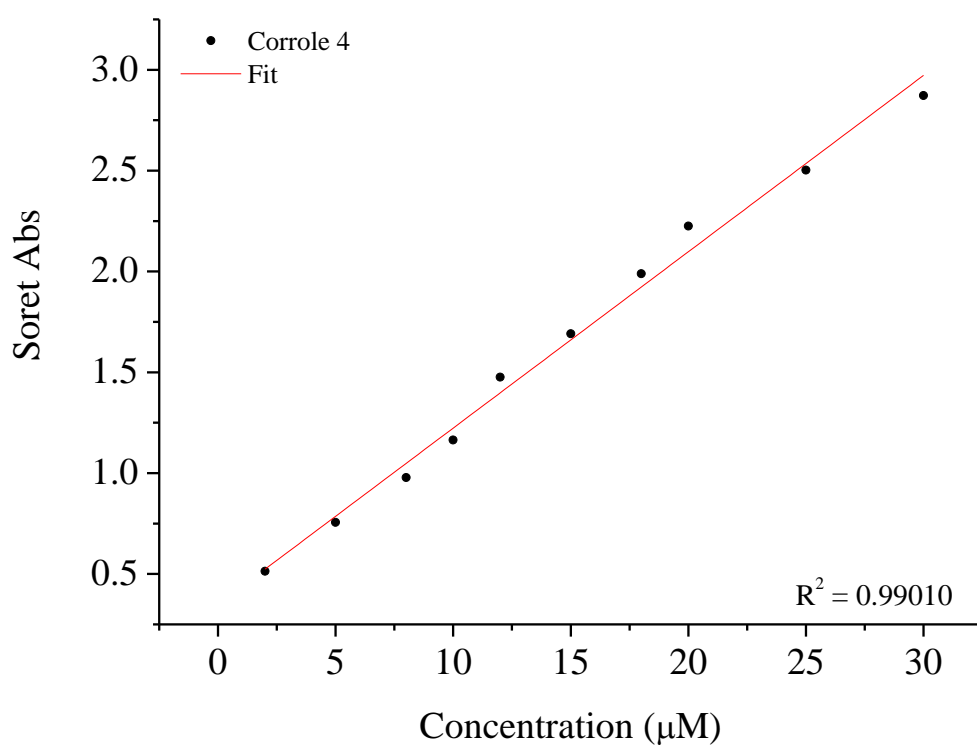
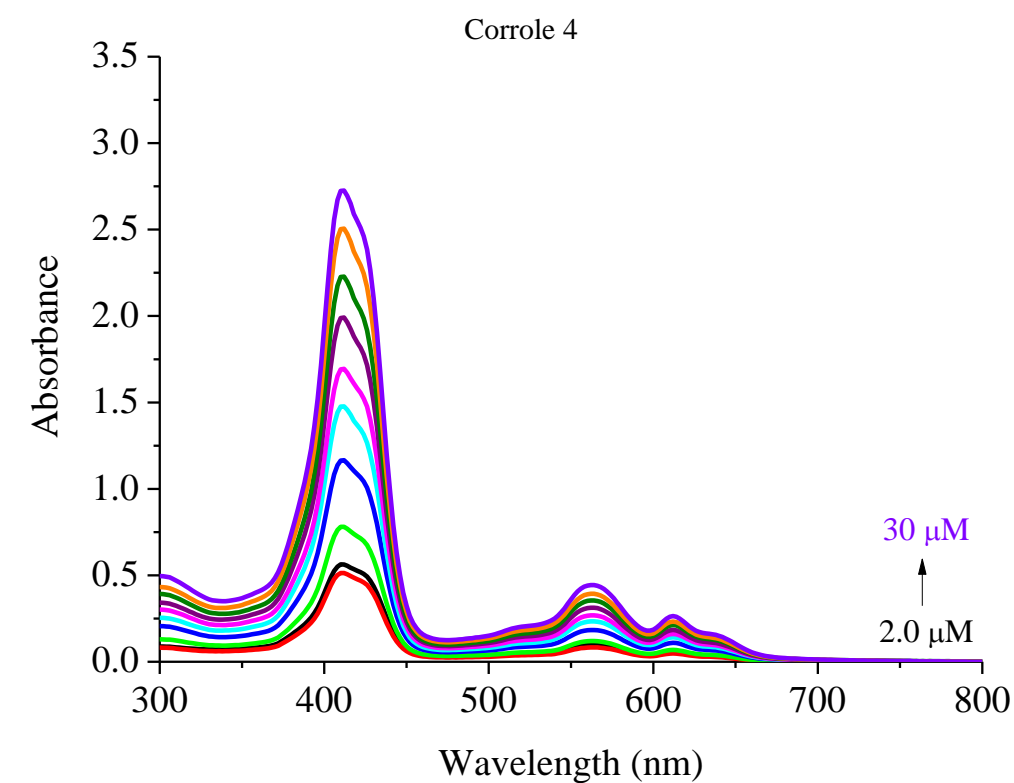
**Figure S19.** (up) Aggregation behavior of corrole 1 in DCM solution and (down)  $\text{Abs}_{\text{Soret}}$  versus concentration plot.



**Figure S20.** (up) Aggregation behavior of corrole 2 in DCM solution and (down)  $\text{Abs}_{\text{Soret}}$  versus concentration plot.

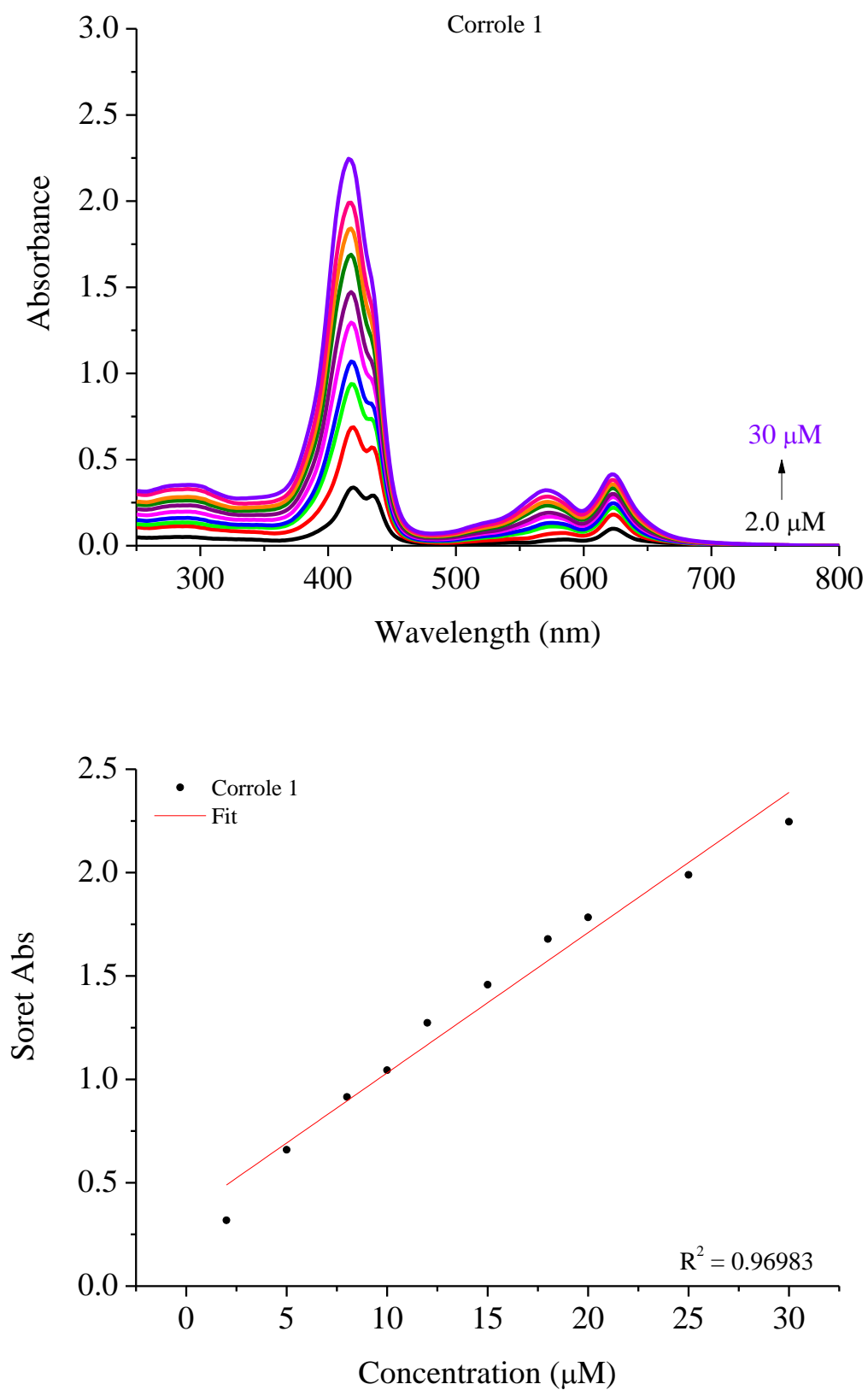


**Figure S21.** (up) Aggregation behavior of corrole **3** in DCM solution and (down)  $\text{Abs}_{\text{Soret}}$  versus concentration plot.

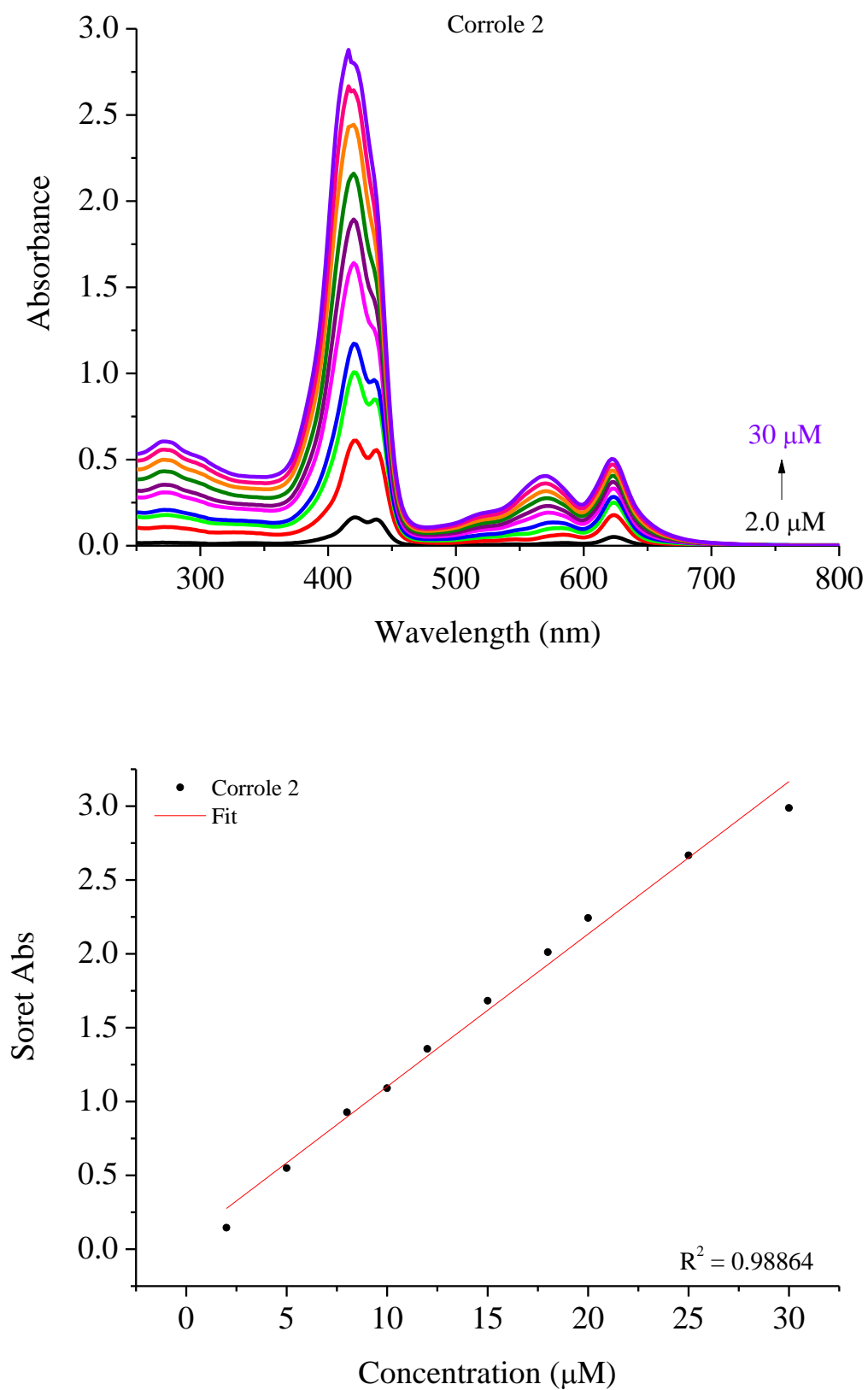


**Figure S22.** (up) Aggregation behavior of corrole **4** in DCM solution and (down)  $\text{Abs}_{\text{Soret}}$  versus concentration plot.

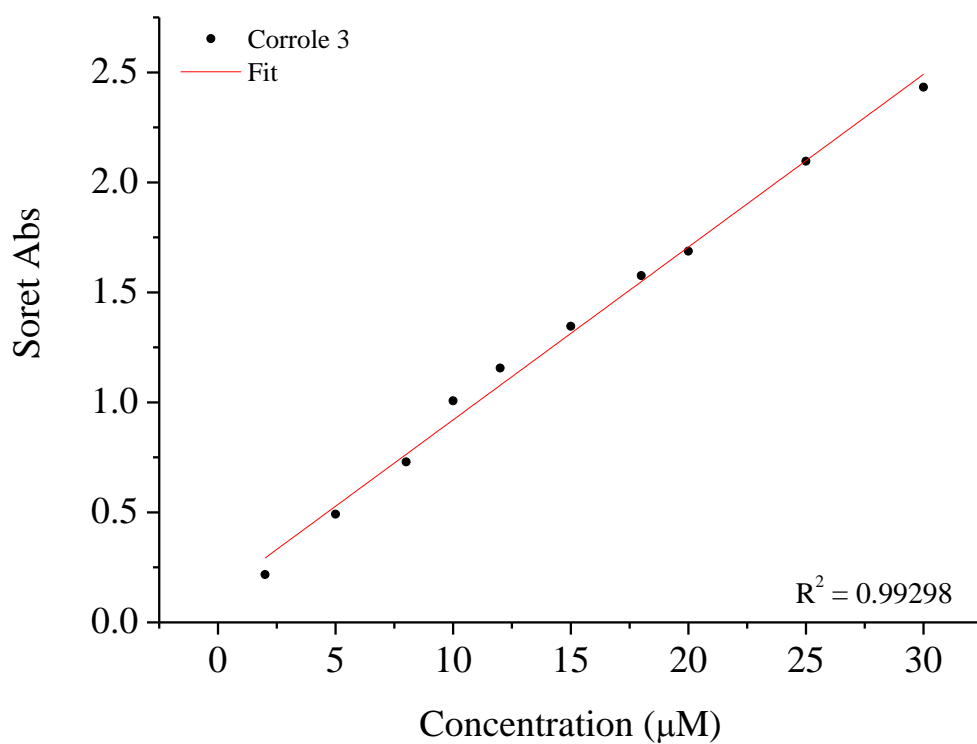
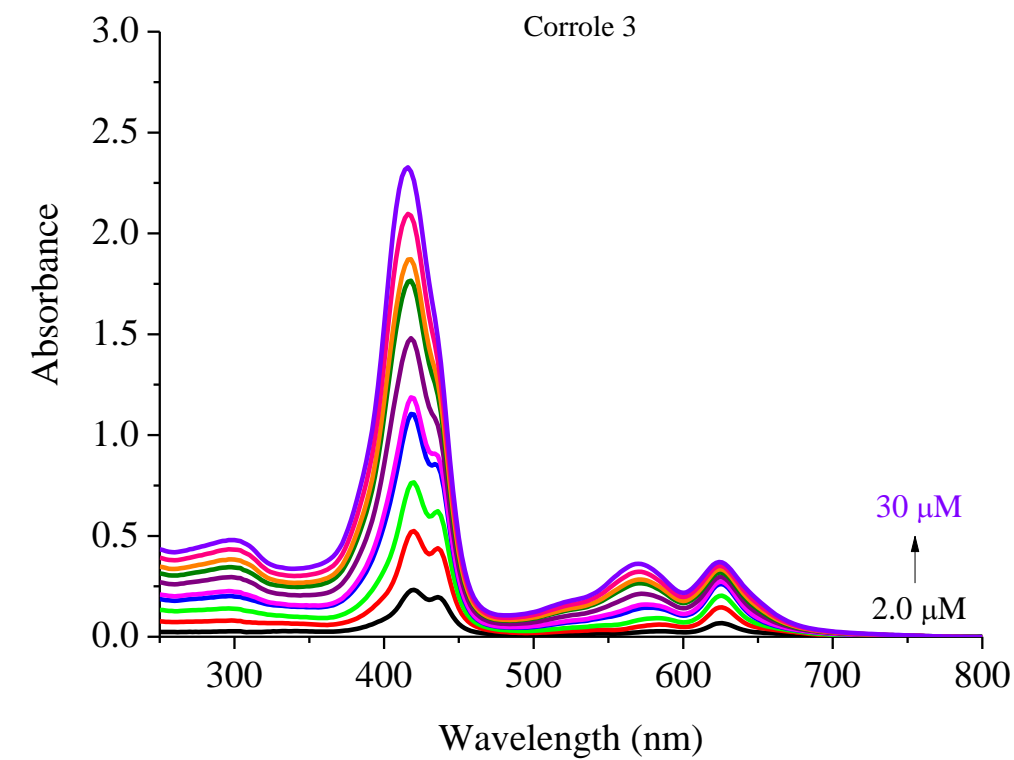




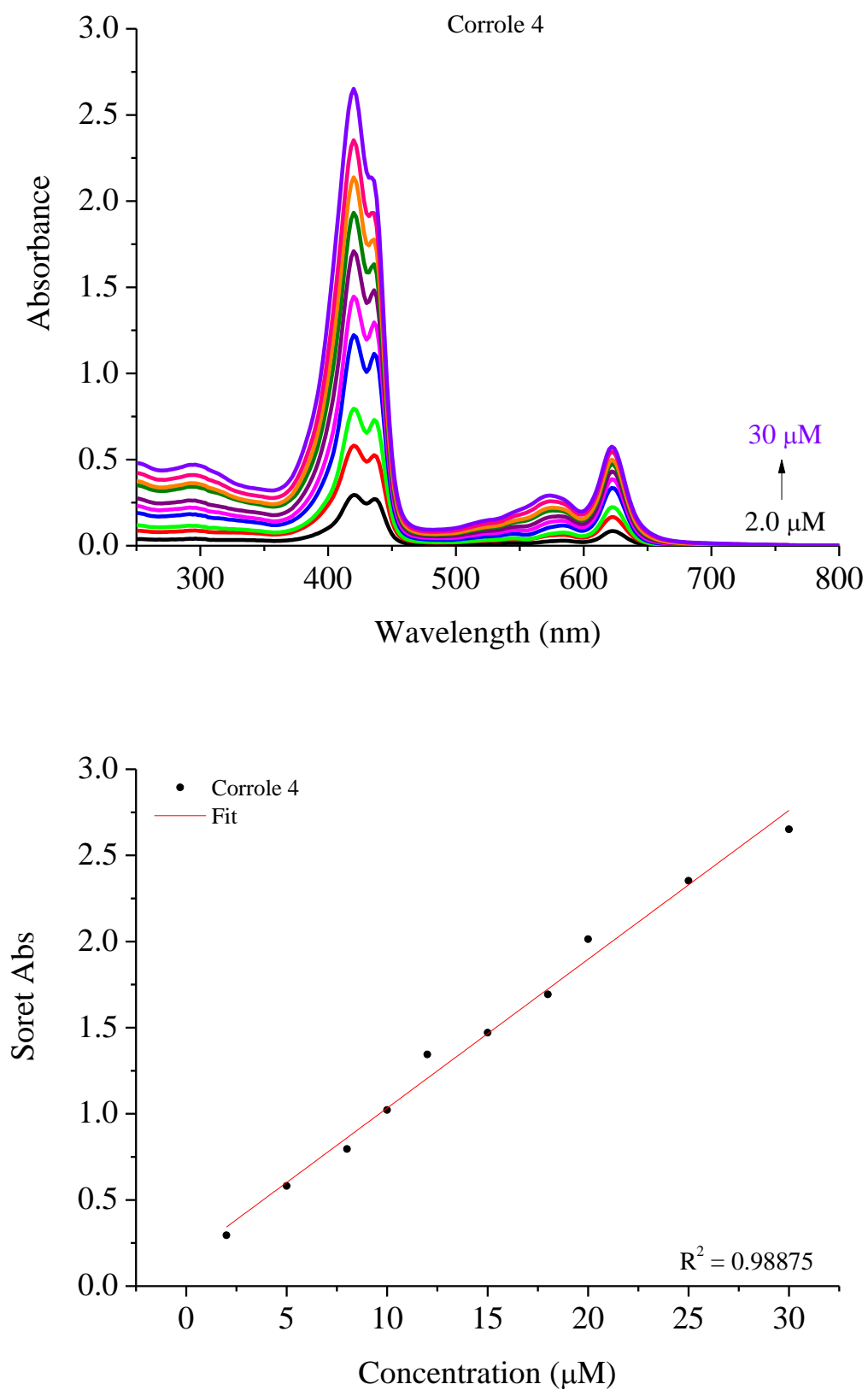
**Figure S23.** (up) Aggregation behavior of corrole 1 in ACN solution and (down)  $\text{Abs}_{\text{Soret}}$  versus concentration plot.



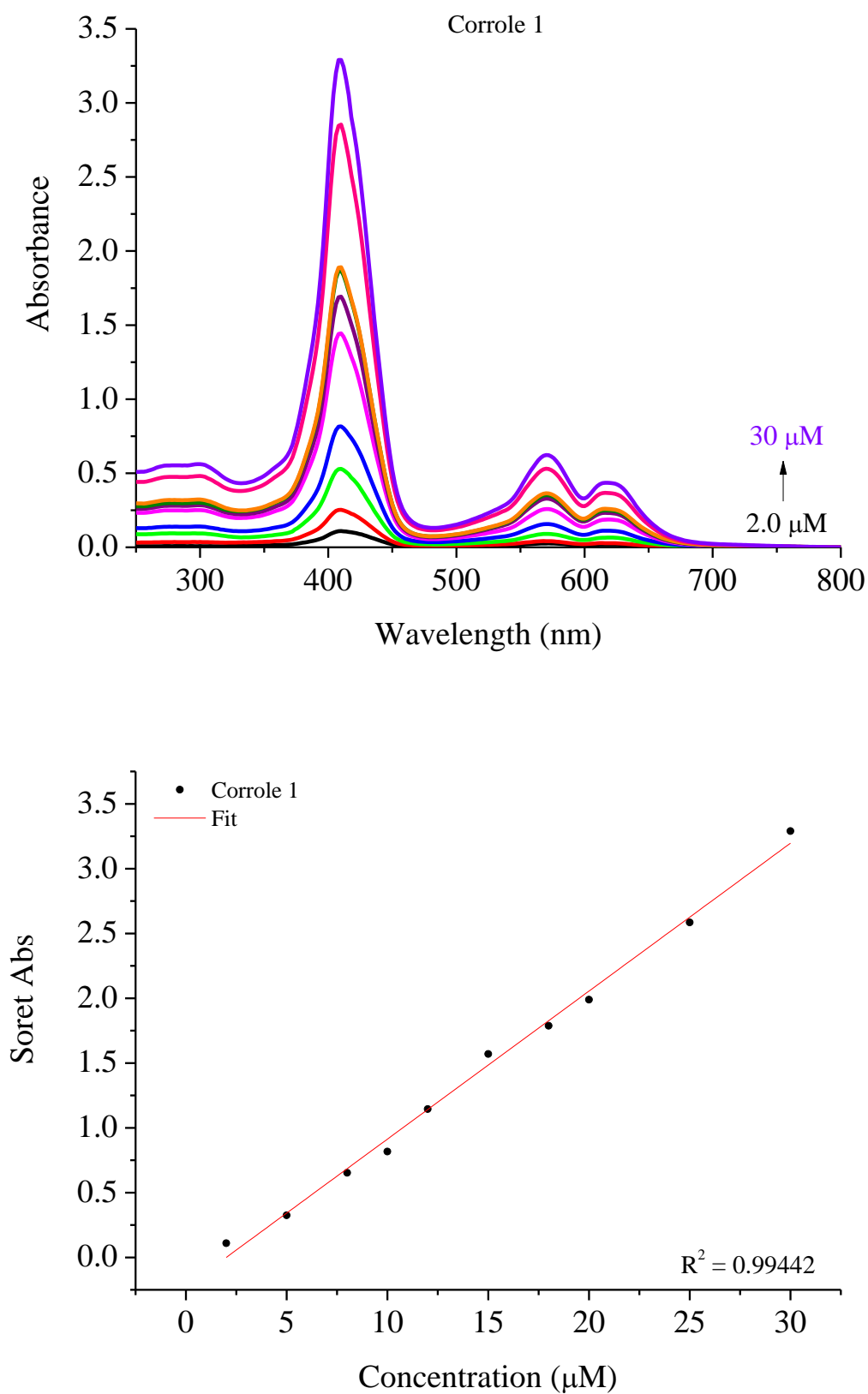
**Figure S24.** (up) Aggregation behavior of corrole **2** in ACN solution and (down)  $\text{Abs}_{\text{Soret}}$  versus concentration plot.



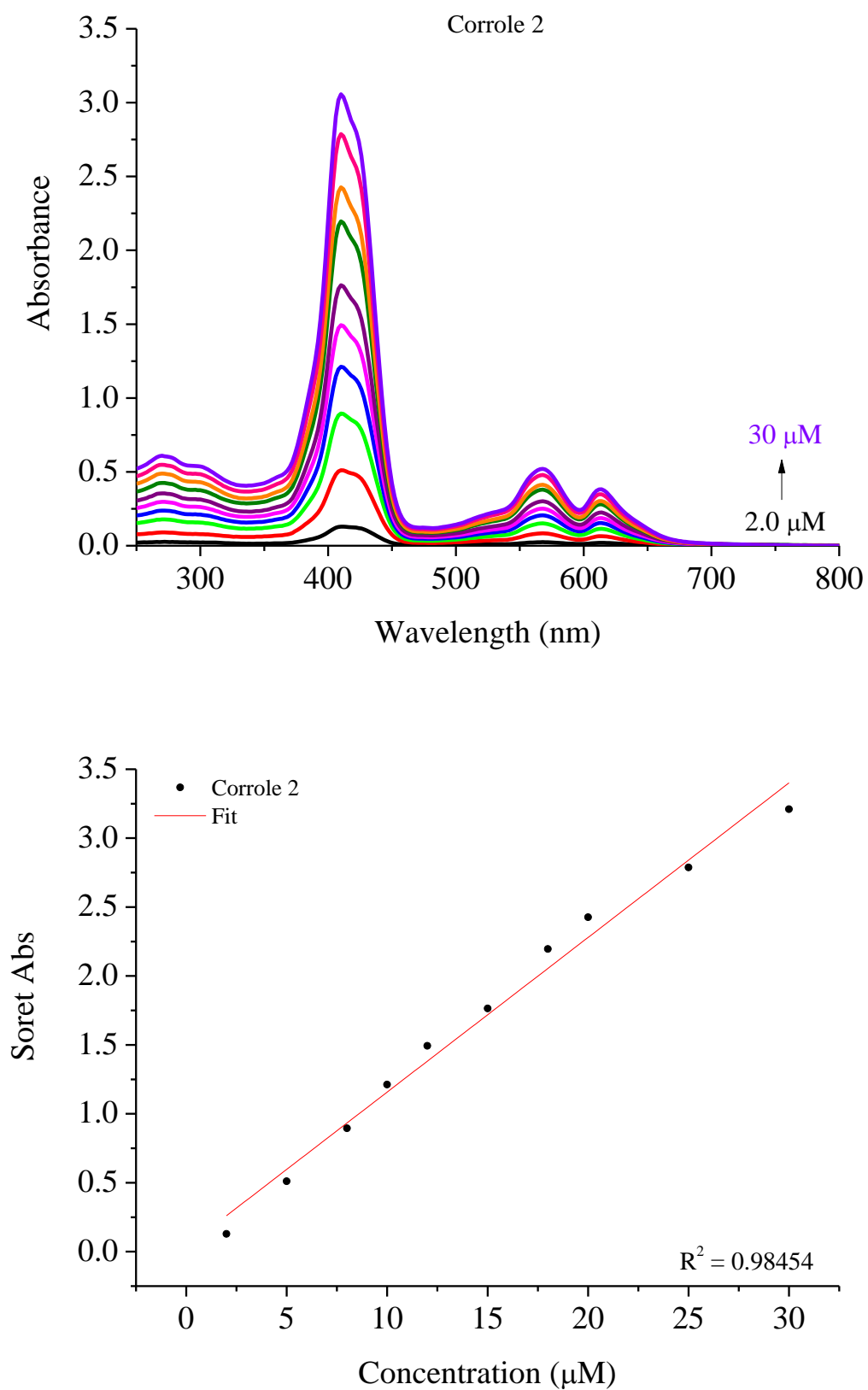
**Figure S25.** (up) Aggregation behavior of corrole **3** in ACN solution and (down)  $\text{Abs}_{\text{Soret}}$  versus concentration plot.



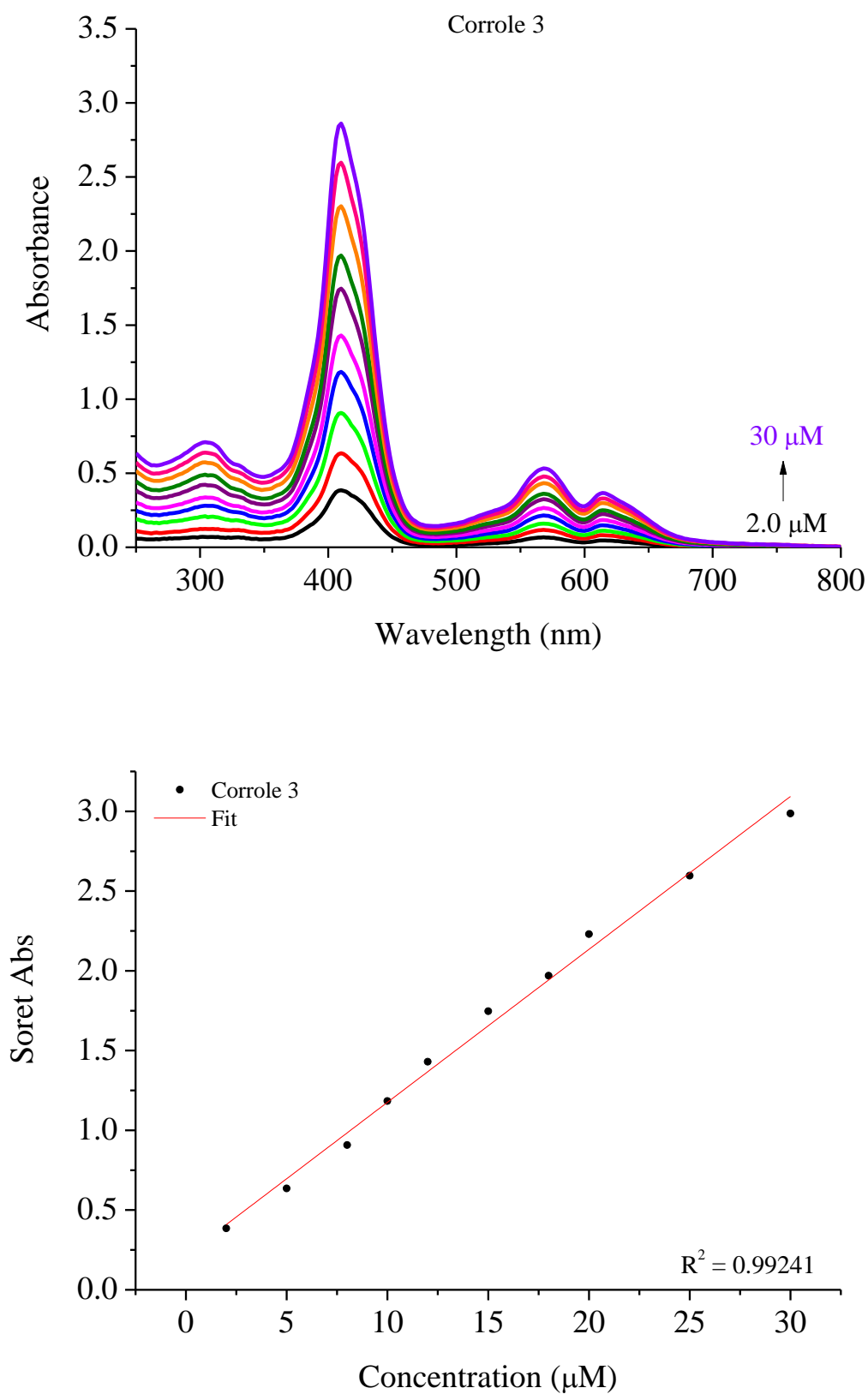
**Figure S26.** (up) Aggregation behavior of corrole 4 in ACN solution and (down)  $\text{Abs}_{\text{Soret}}$  versus concentration plot.



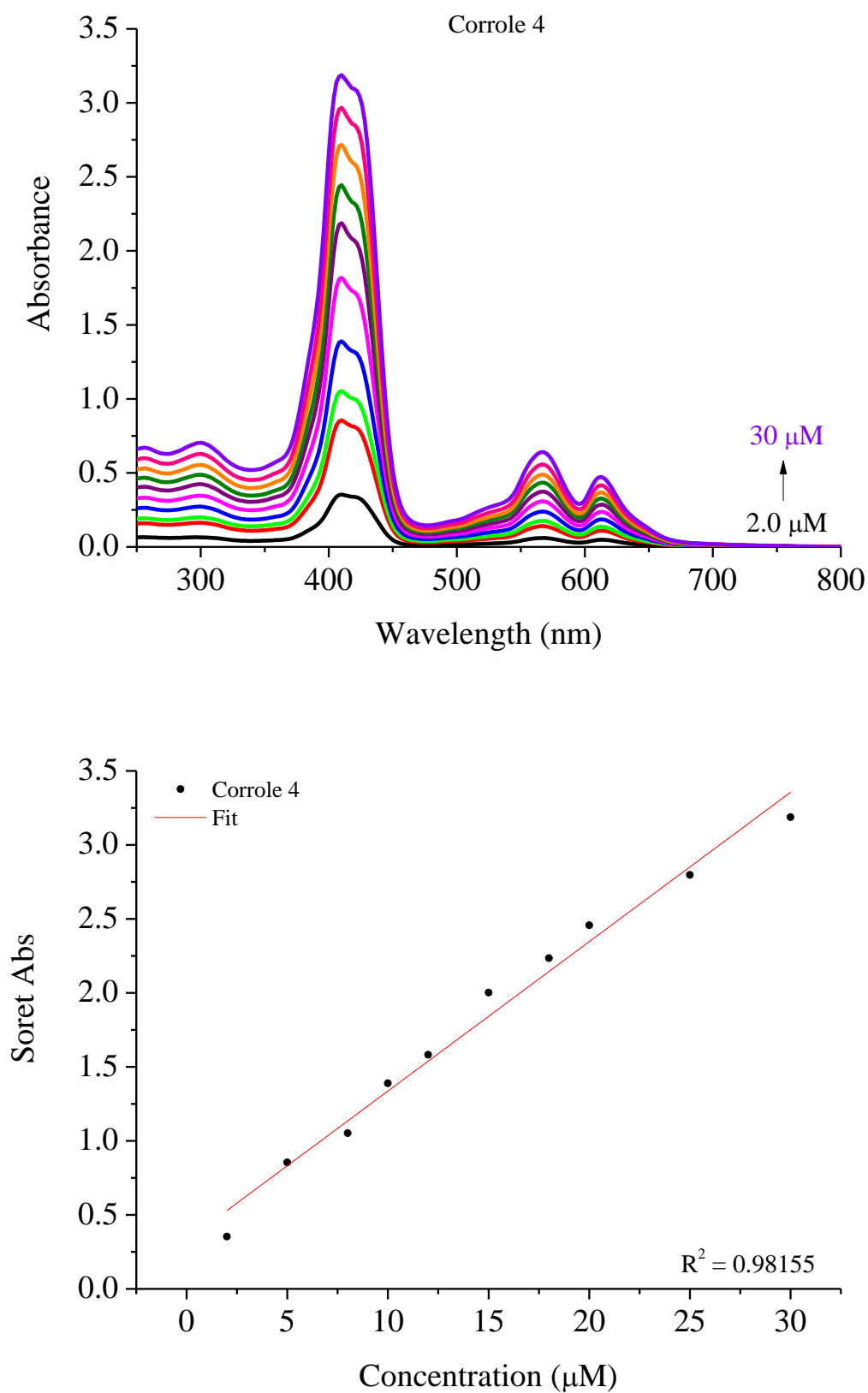
**Figure S27.** (up) Aggregation behavior of corrole 1 in MeOH solution and (down)  $\text{Abs}_{\text{Soret}}$  versus concentration plot.



**Figure S28.** (up) Aggregation behavior of corrole **2** in MeOH solution and (down) Abs<sub>Soret</sub> versus concentration plot.

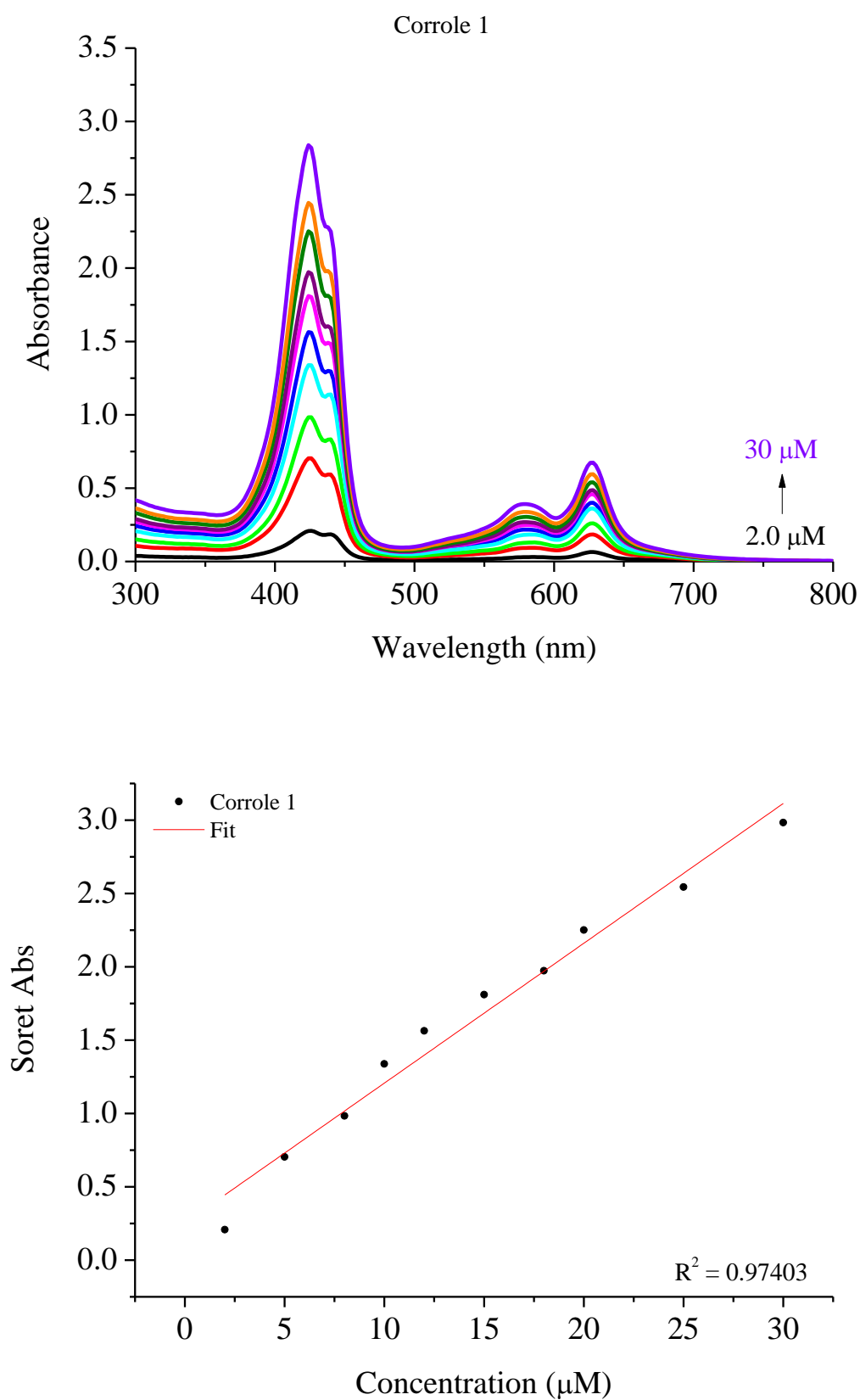


**Figure S29.** (up) Aggregation behavior of corrole 3 in MeOH solution and (down)  $\text{Abs}_{\text{Soret}}$  versus concentration plot.

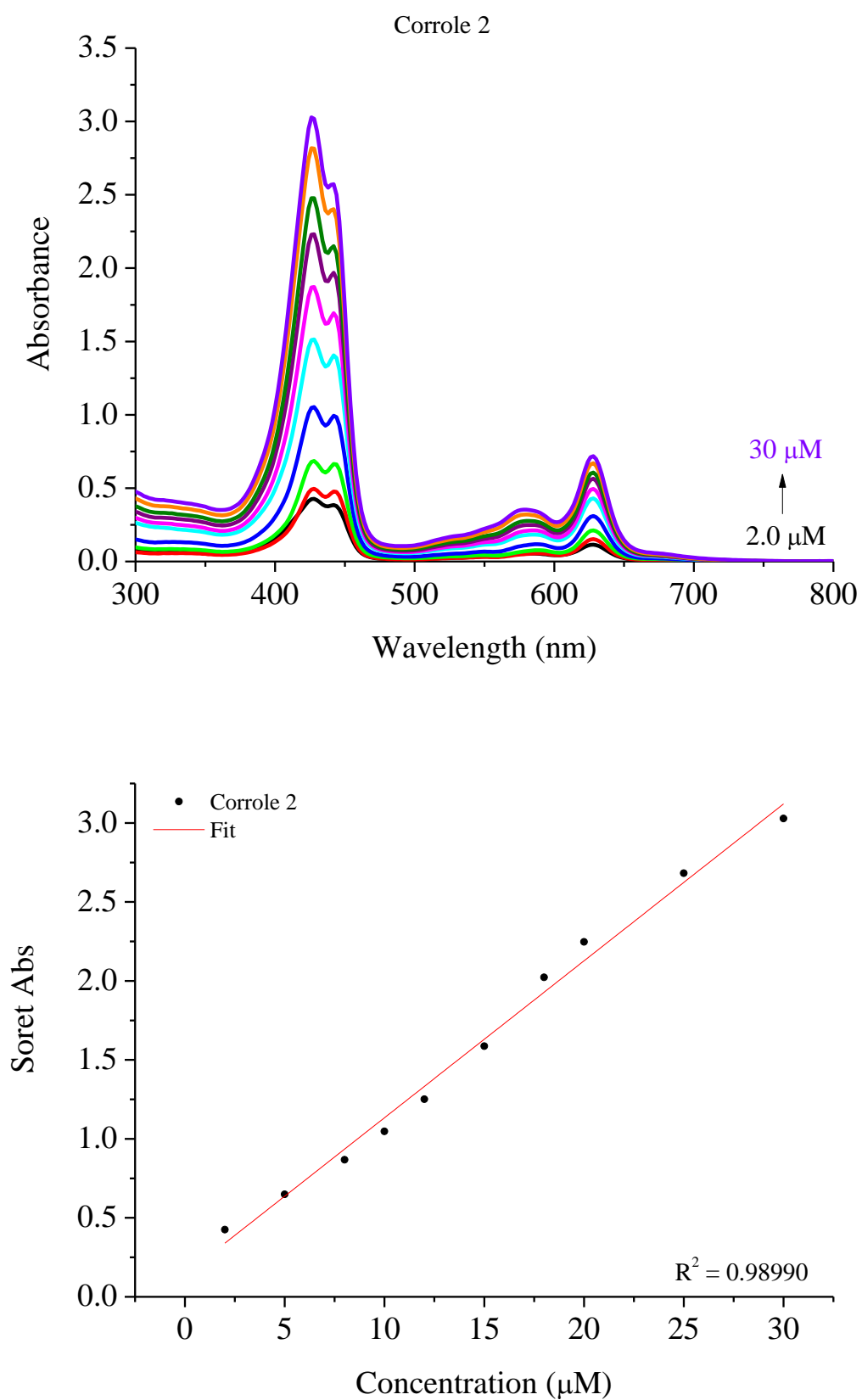


**Figure S30.** (up) Aggregation behavior of corrole **4** in MeOH solution and (down)  $\text{Abs}_{\text{Soret}}$  versus concentration plot.

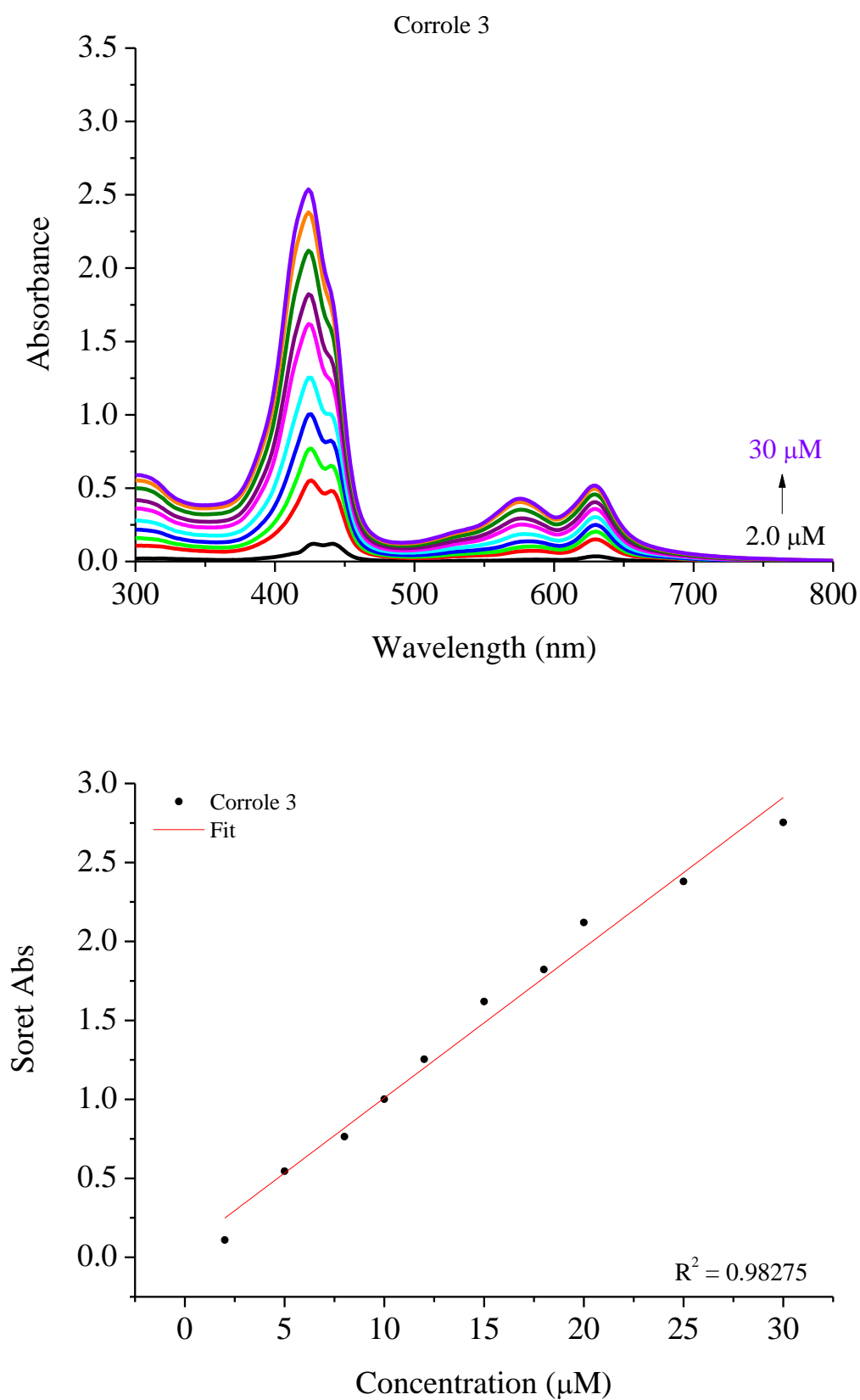




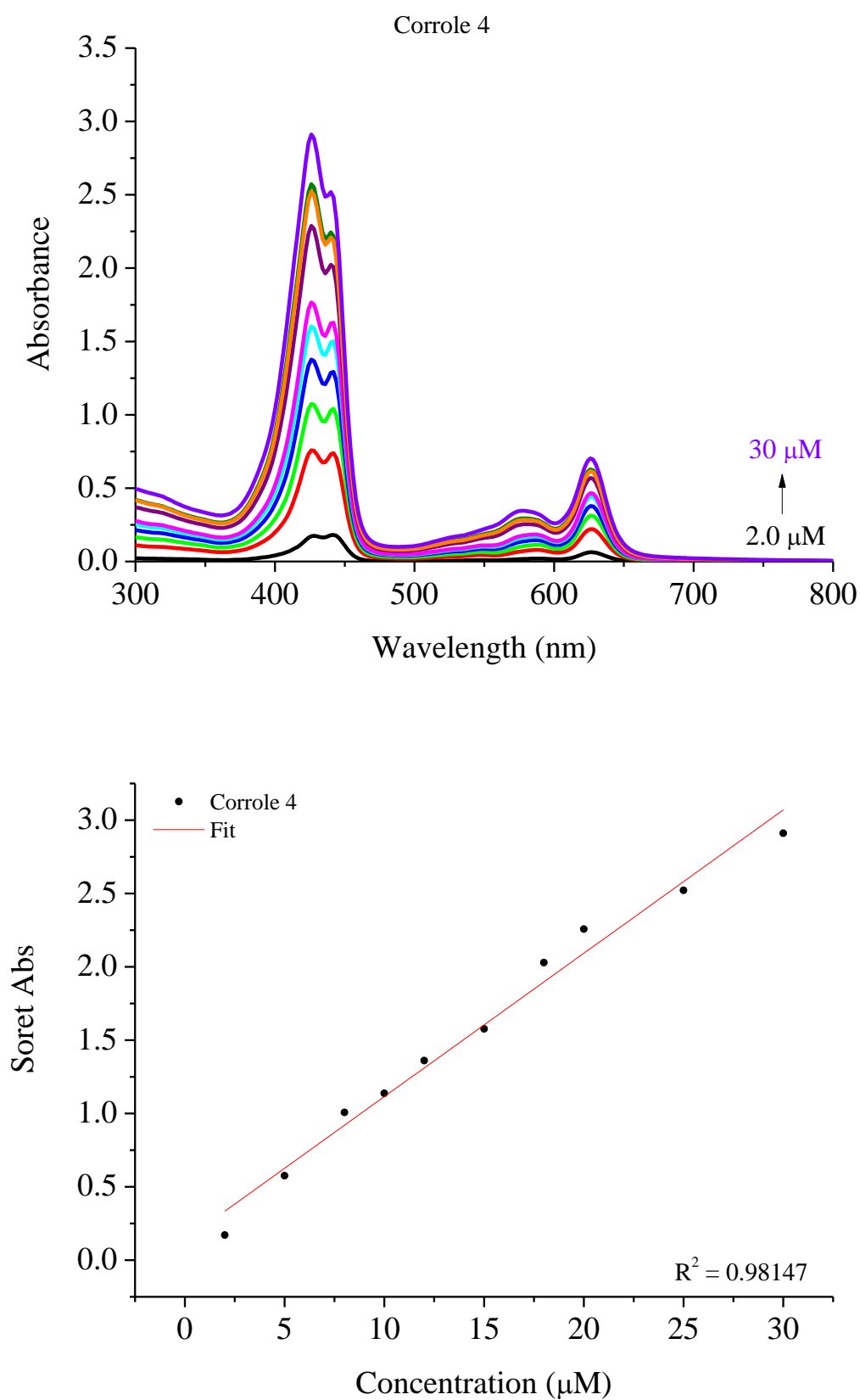
**Figure S31.** (up) Aggregation behavior of corrole 1 in DMSO solution and (down)  $\text{Abs}_{\text{Soret}}$  versus concentration plot.



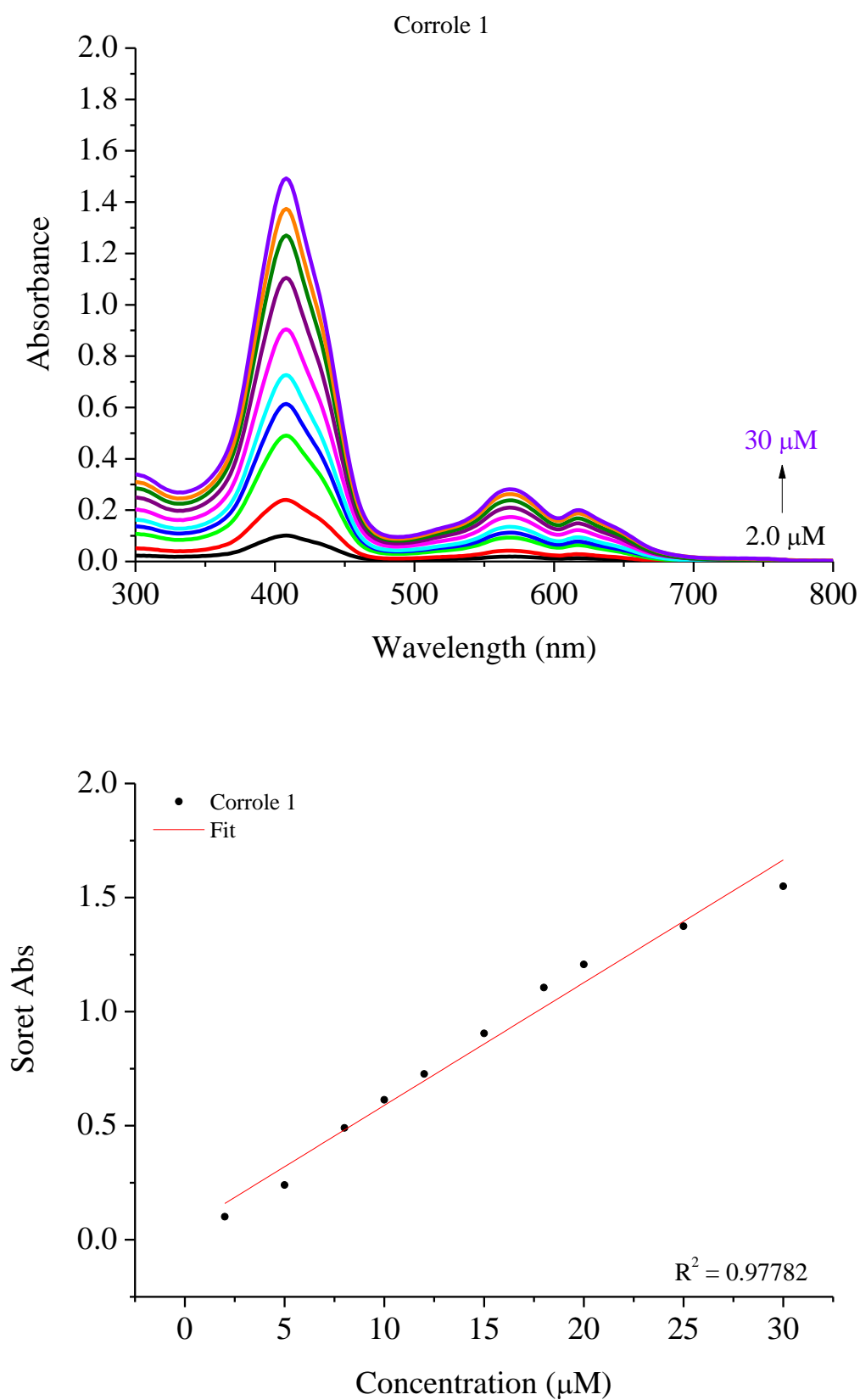
**Figure S32.** (up) Aggregation behavior of corrole **2** in DMSO solution and (down)  $\text{Abs}_{\text{Soret}}$  versus concentration plot.



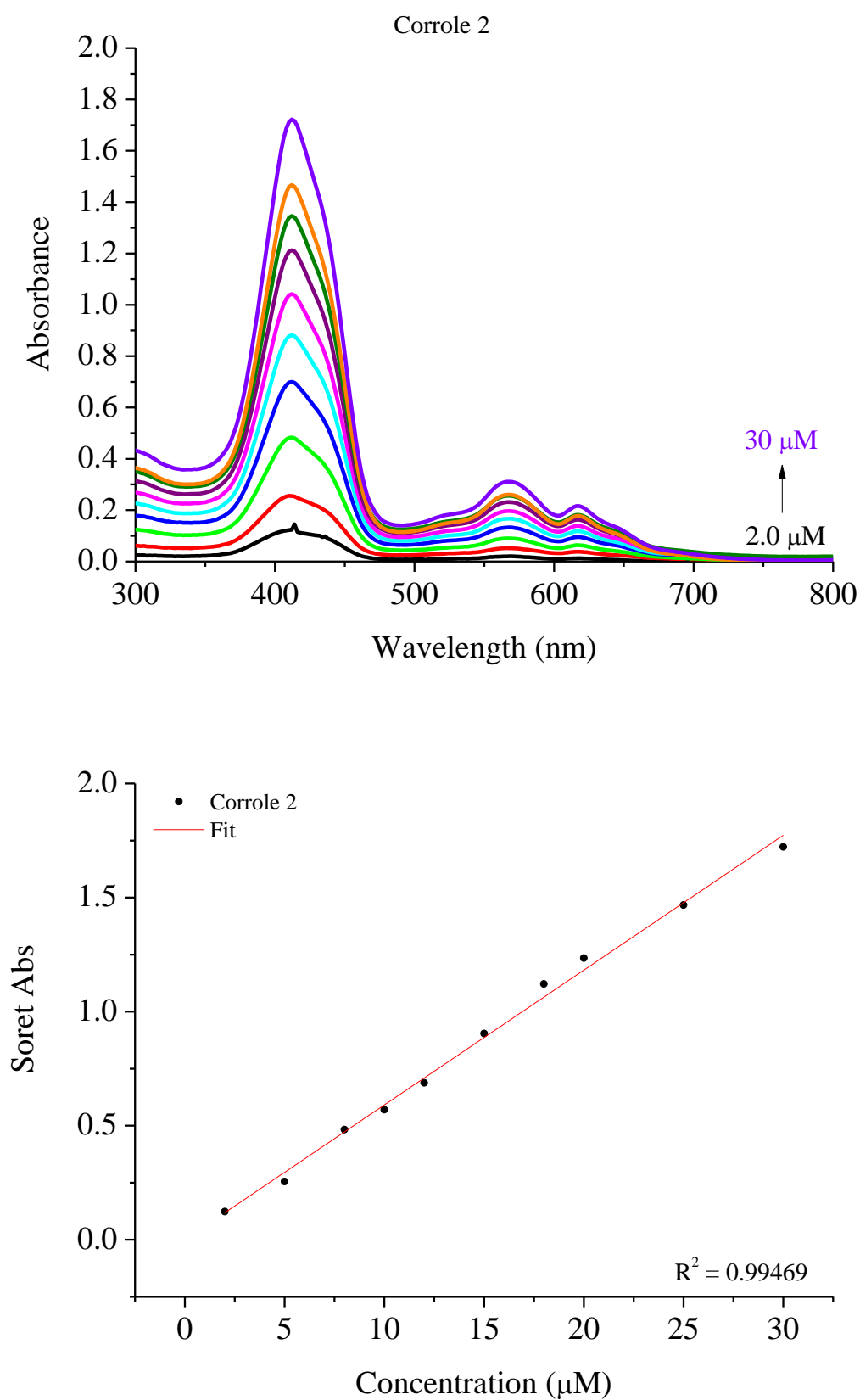
**Figure S33.** (up) Aggregation behavior of corrole **3** in DMSO solution and (down)  $\text{Abs}_{\text{Soret}}$  versus concentration plot.



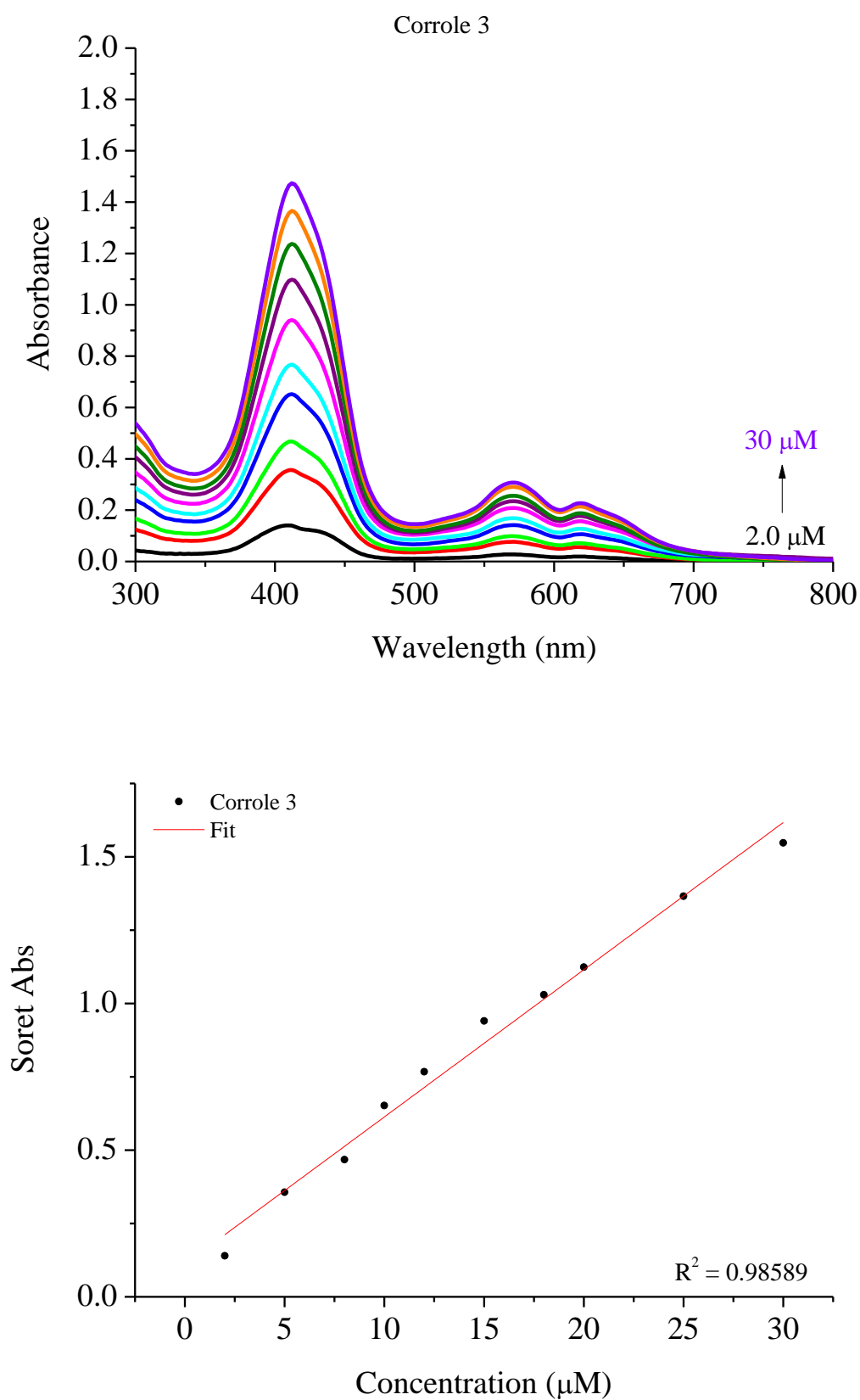
**Figure S34.** (up) Aggregation behavior of corrole 4 in DMSO solution and (down)  $\text{Abs}_{\text{Soret}}$  versus concentration plot.



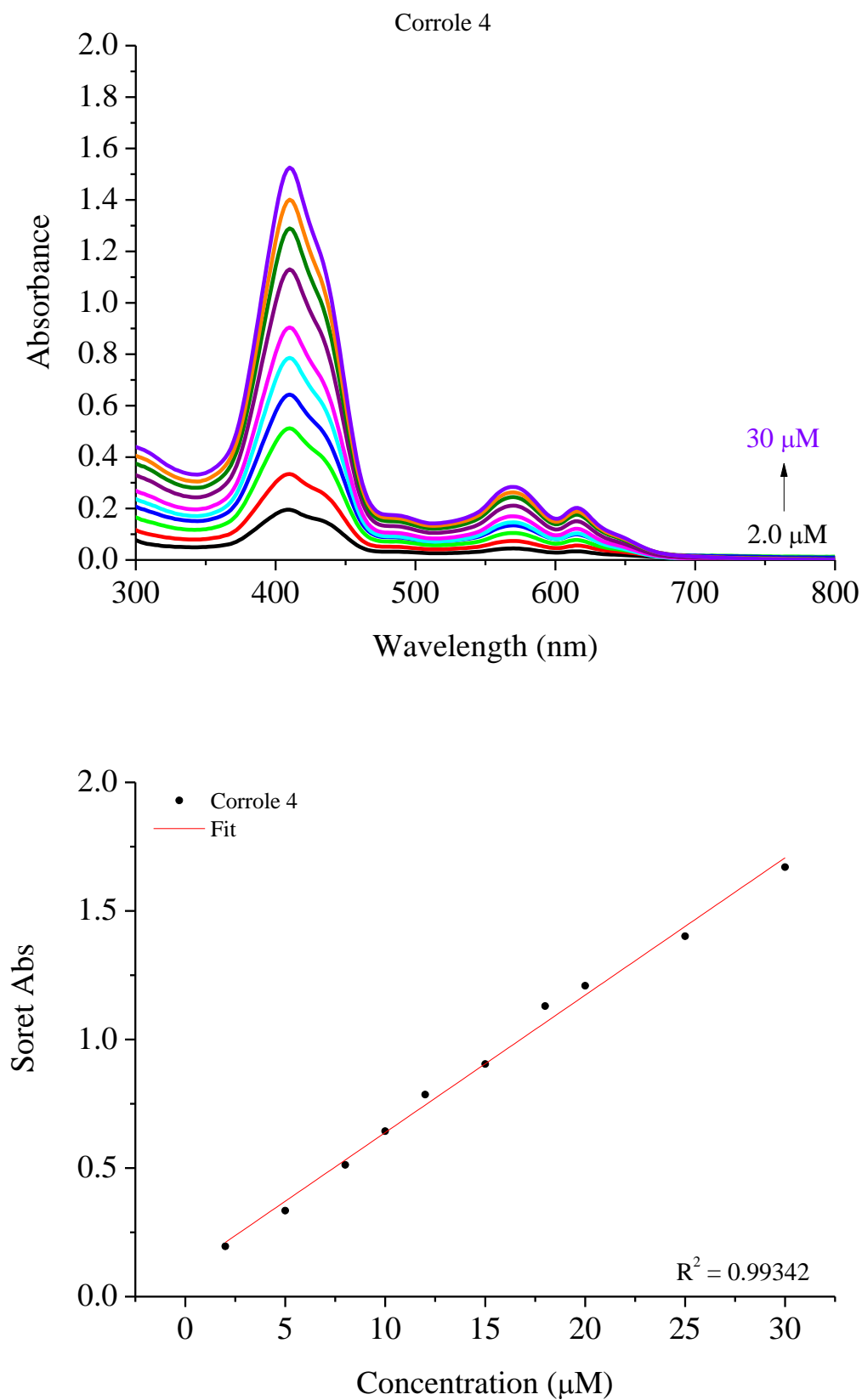
**Figure S35.** (up) Aggregation behavior of corrole 1 in DMSO(5%)/Tris-HCl pH 7.4 buffered mixture solution and (down) Abs<sub>Soret</sub> versus concentration plot.



**Figure S36.** (up) Aggregation behavior of corrole 2 in DMSO(5%)/Tris-HCl pH 7.4 buffered mixture solution and (down)  $\text{Abs}_{\text{Soret}}$  versus concentration plot.

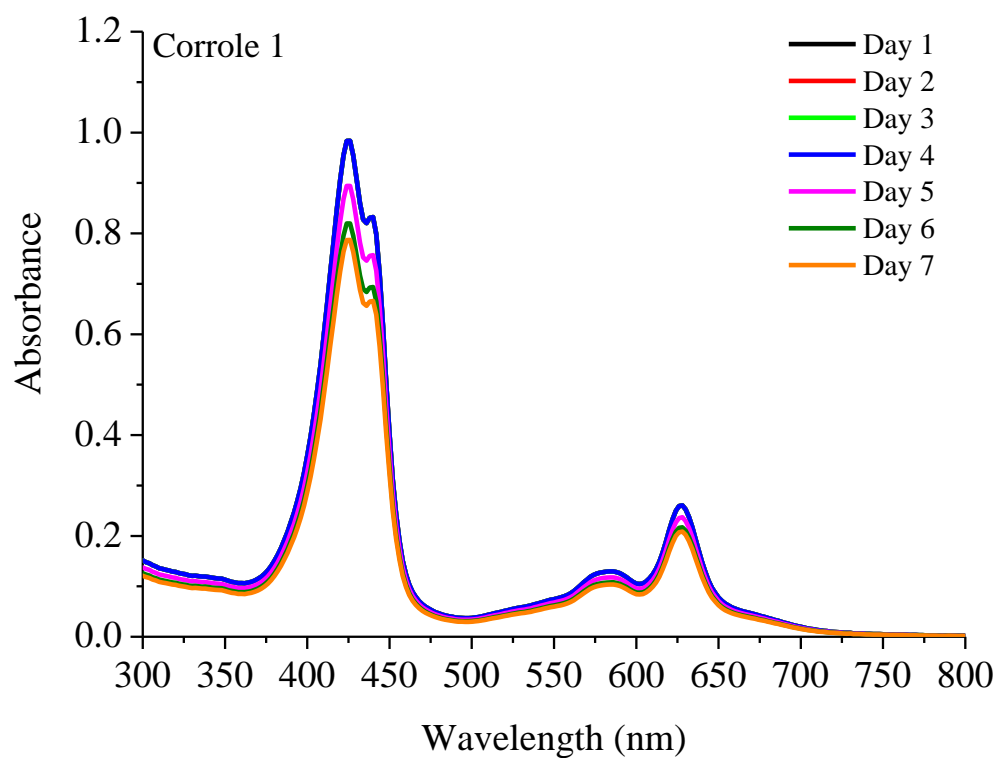


**Figure S37.** (up) Aggregation behavior of corrole 3 in DMSO(5%)/Tris-HCl pH 7.4 buffered mixture solution and (down) Abs<sub>Soret</sub> versus concentration plot.

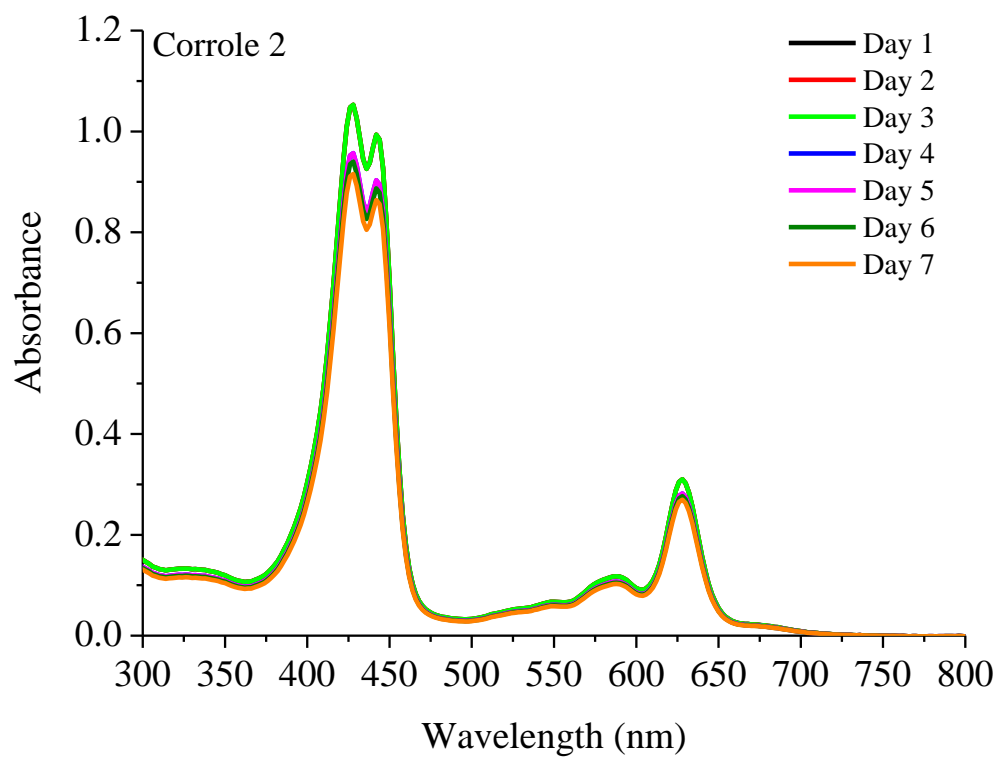


**Figure S38.** (up) Aggregation behavior of corrole 4 in DMSO(5%)/Tris-HCl pH 7.4 buffered mixture solution and (down)  $\text{Abs}_{\text{Soret}}$  versus concentration plot.

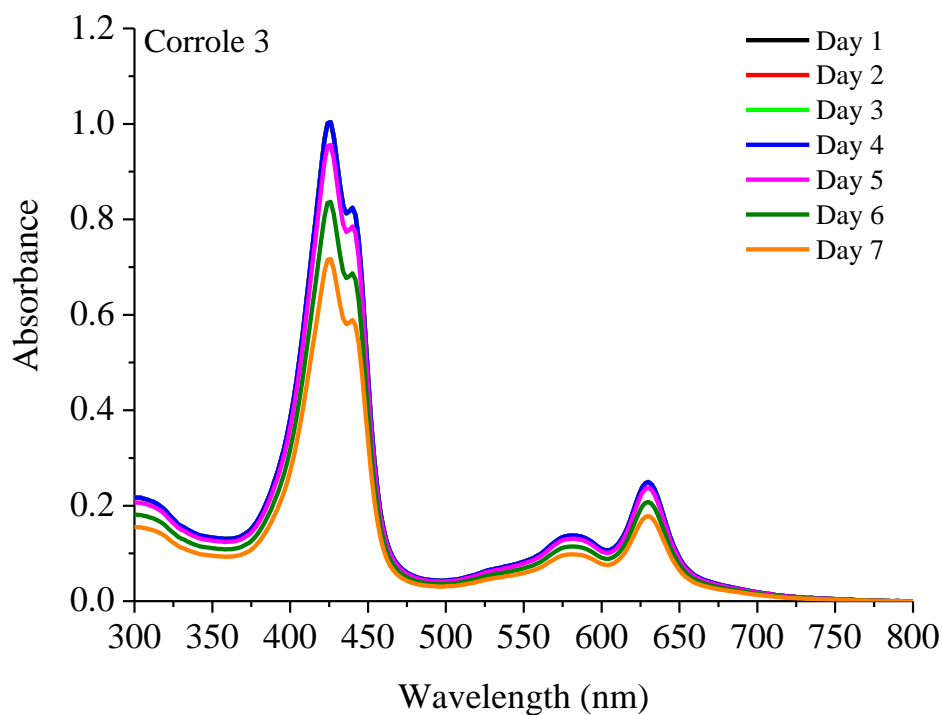




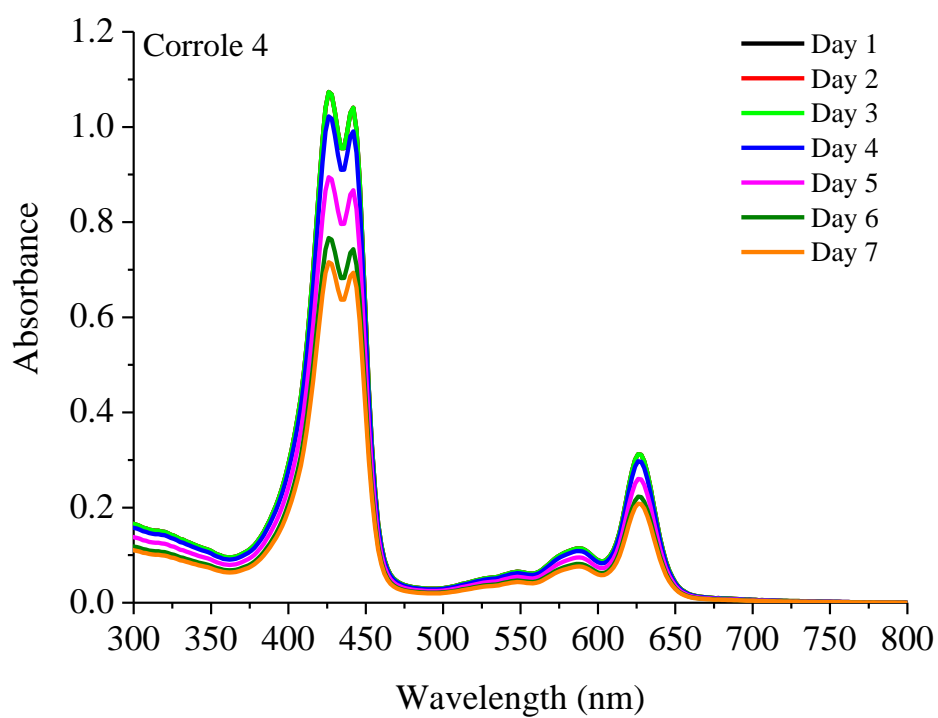
**Figure S39.** Stability assay of corrole 1 in DMSO solution.



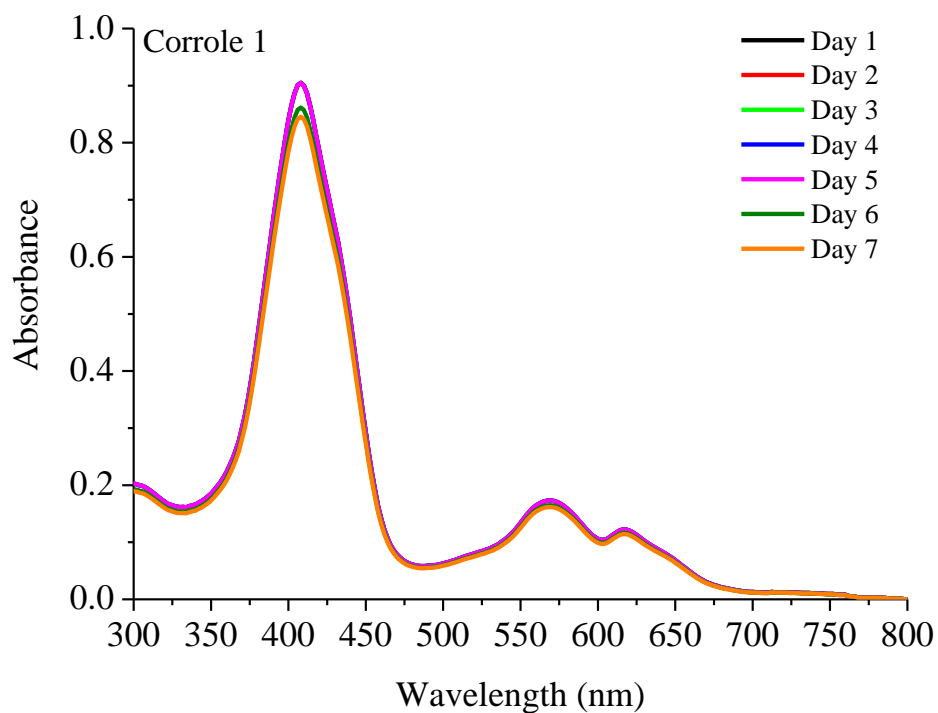
**Figure S40.** Stability assay of corrole 2 in DMSO solution.



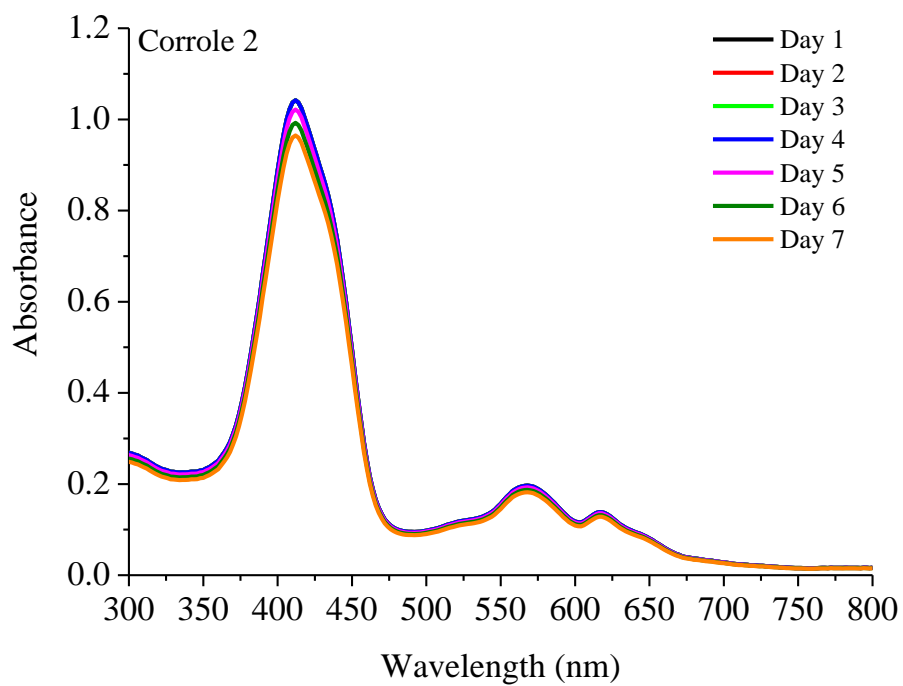
**Figure S41.** Stability assay of corrole **3** in DMSO solution.



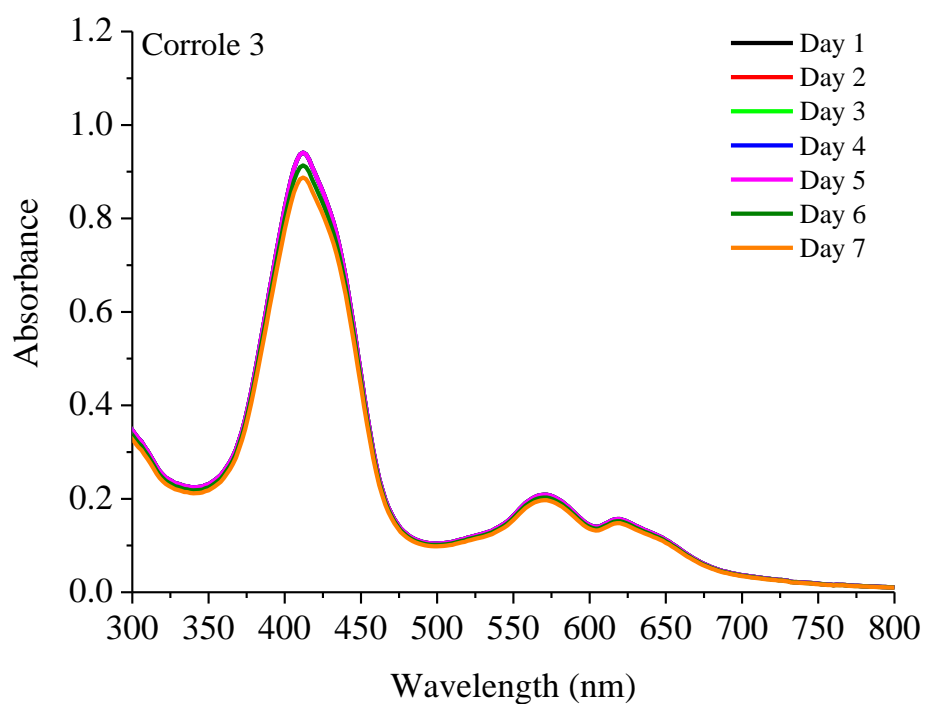
**Figure S42.** Stability assay of corrole **4** in DMSO solution.



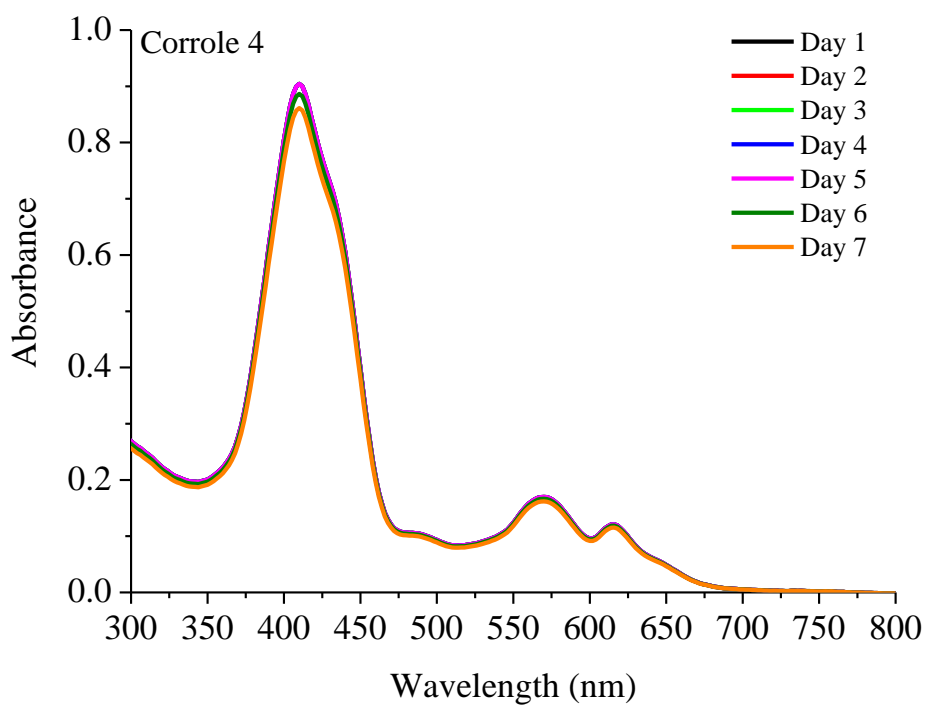
**Figure S43.** Stability assay of corrole 1 in DMSO(5%)/Tris-HCl pH 7.4 buffered mixture solution.



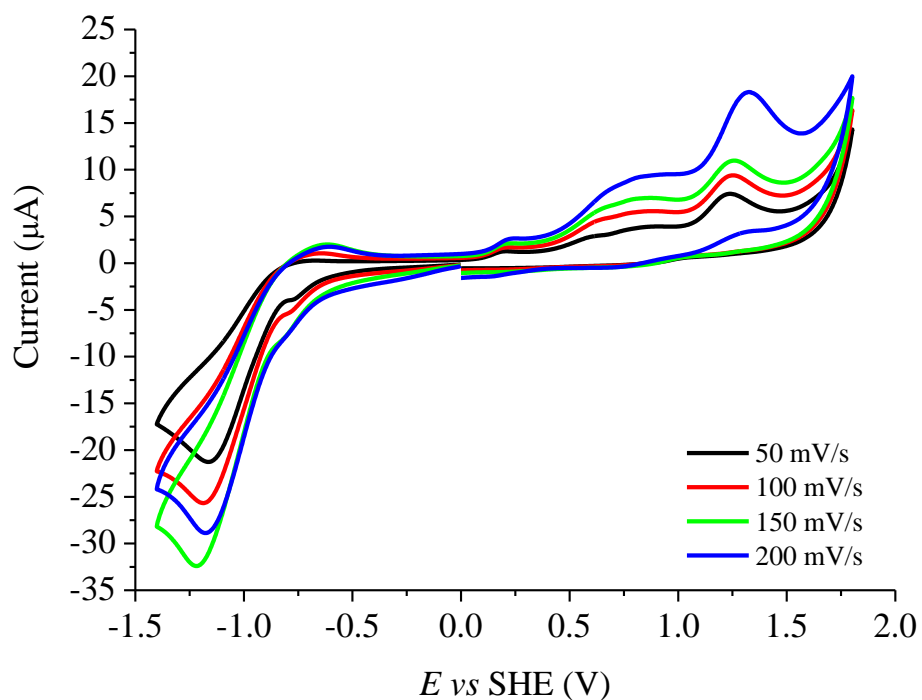
**Figure S44.** Stability assay of corrole 2 in DMSO(5%)/Tris-HCl pH 7.4 buffered mixture solution.



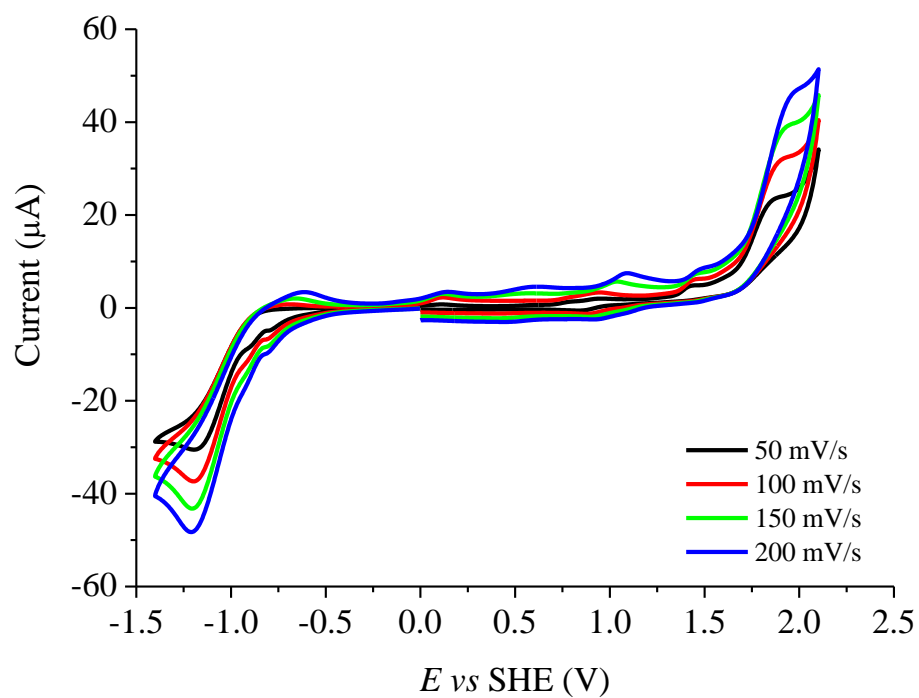
**Figure S45.** Stability assay of corrole 3 in DMSO(5%)/Tris-HCl pH 7.4 buffered mixture solution.



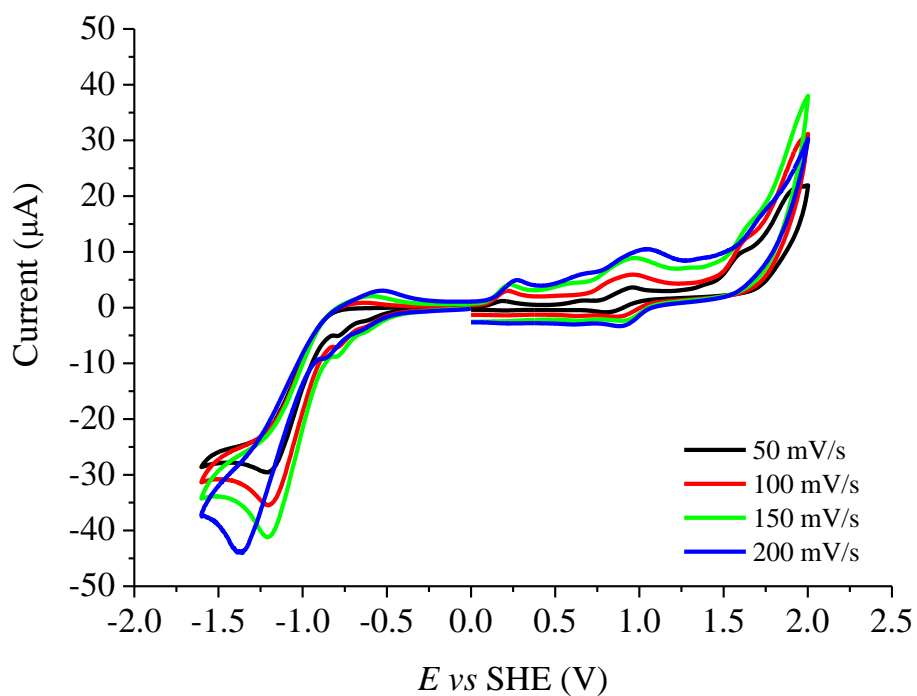
**Figure S46.** Stability assay of corrole 4 in DMSO(5%)/Tris-HCl pH 7.4 buffered mixture solution.



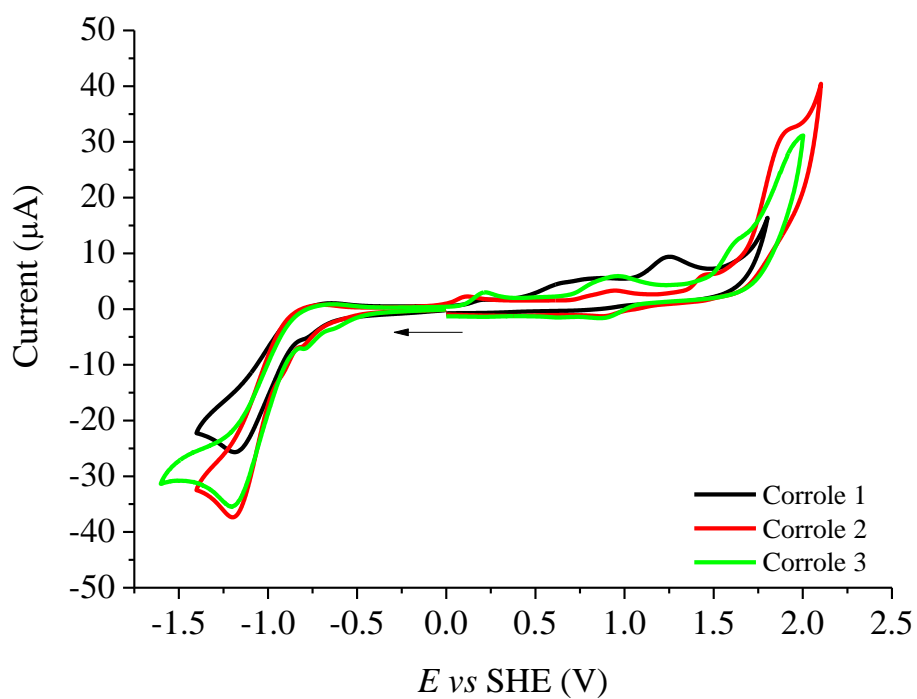
**Figure S47.** Cyclic voltammetry analysis of corrole **1** in dry DCM solution, using 0.1 M TBAPF<sub>6</sub> as support electrolyte.



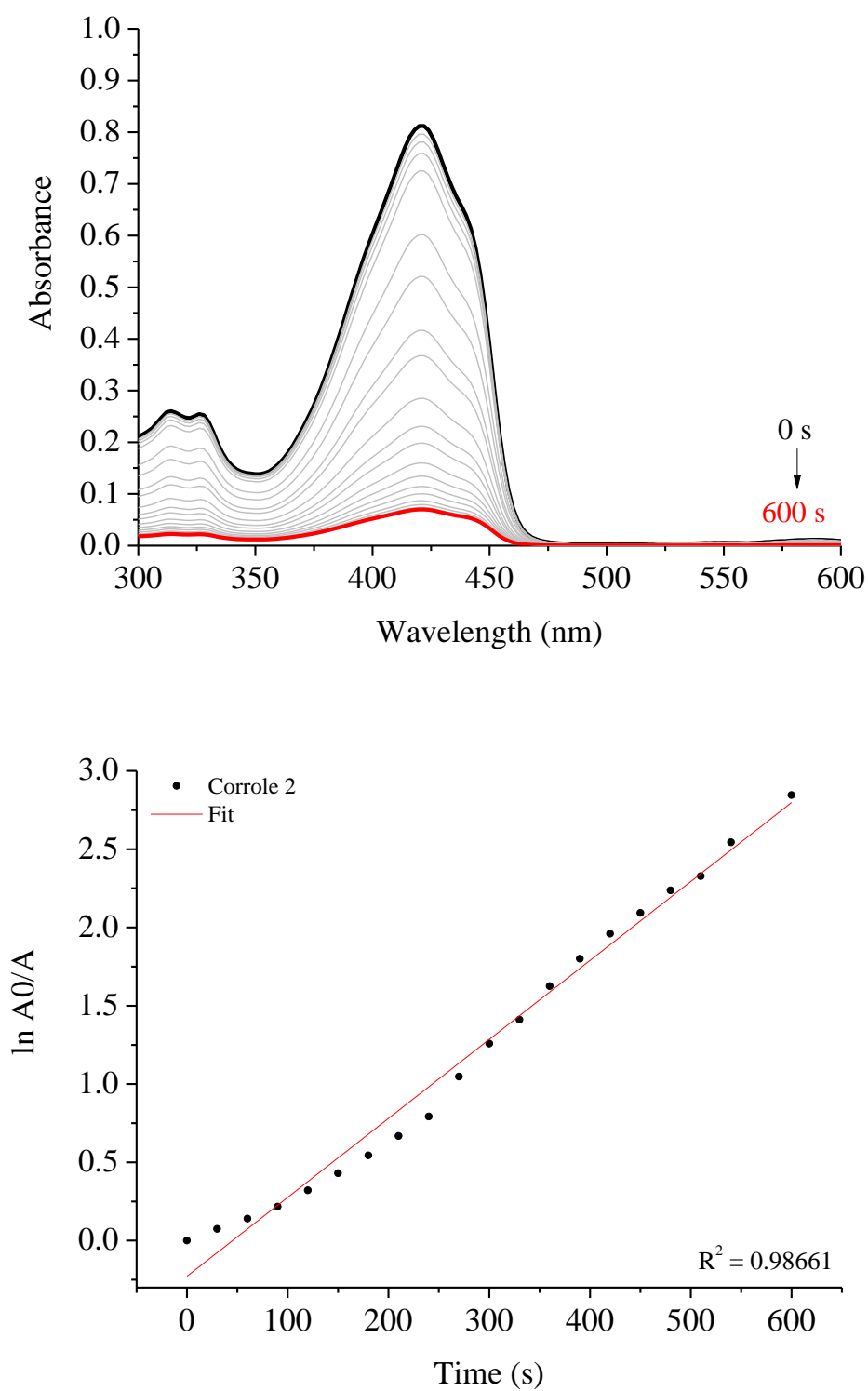
**Figure S48.** Cyclic voltammetry analysis of corrole **2** in dry DCM solution, using 0.1 M TBAPF<sub>6</sub> as support electrolyte.



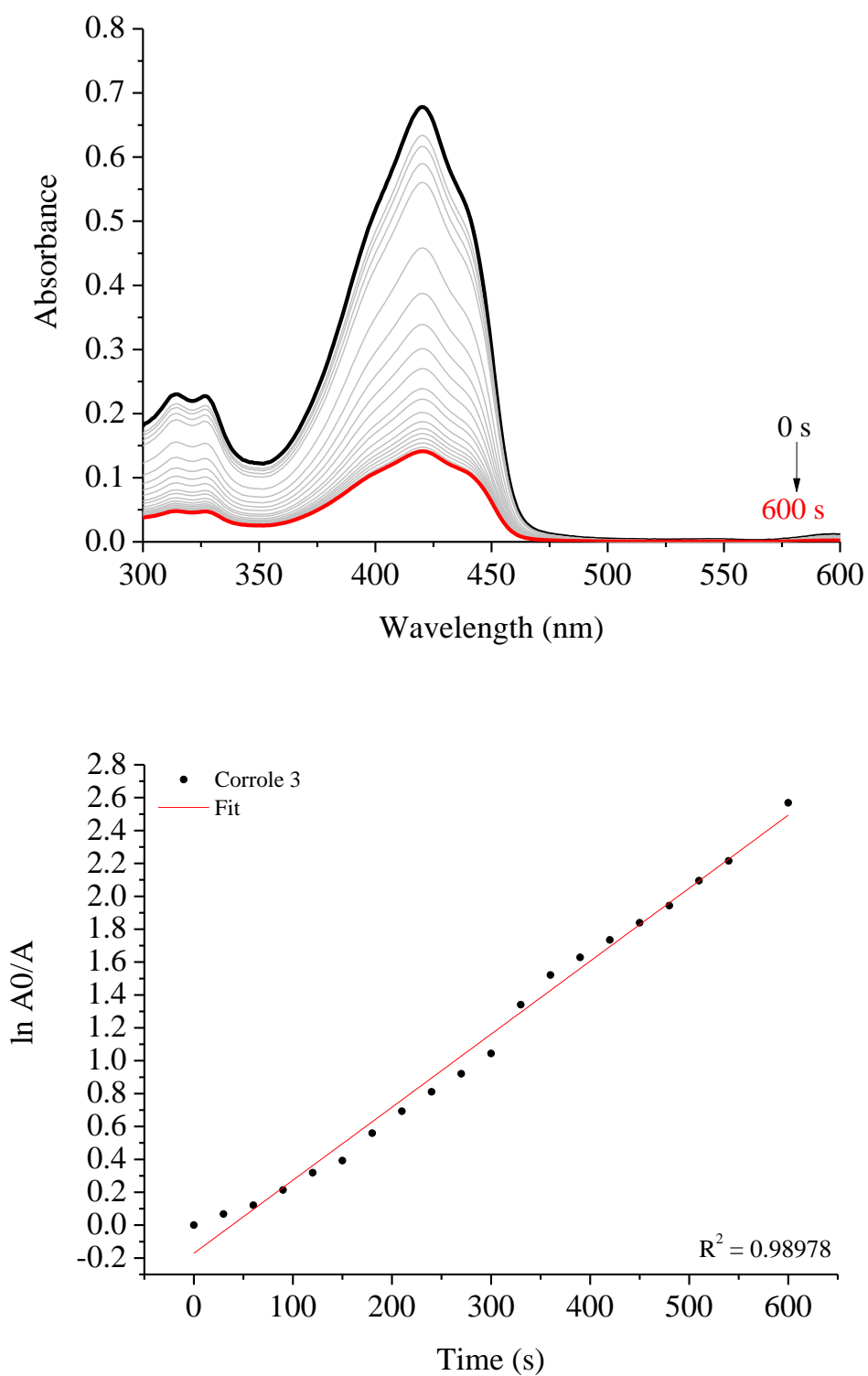
**Figure S49.** Cyclic voltammetry analysis of corrole **3** in dry DCM solution, using 0.1 M TBAPF<sub>6</sub> as support electrolyte.



**Figure S50.** Cyclic voltammetry analysis of corrole **4** in dry DCM solution, using 0.1 M TBAPF<sub>6</sub> as support electrolyte.

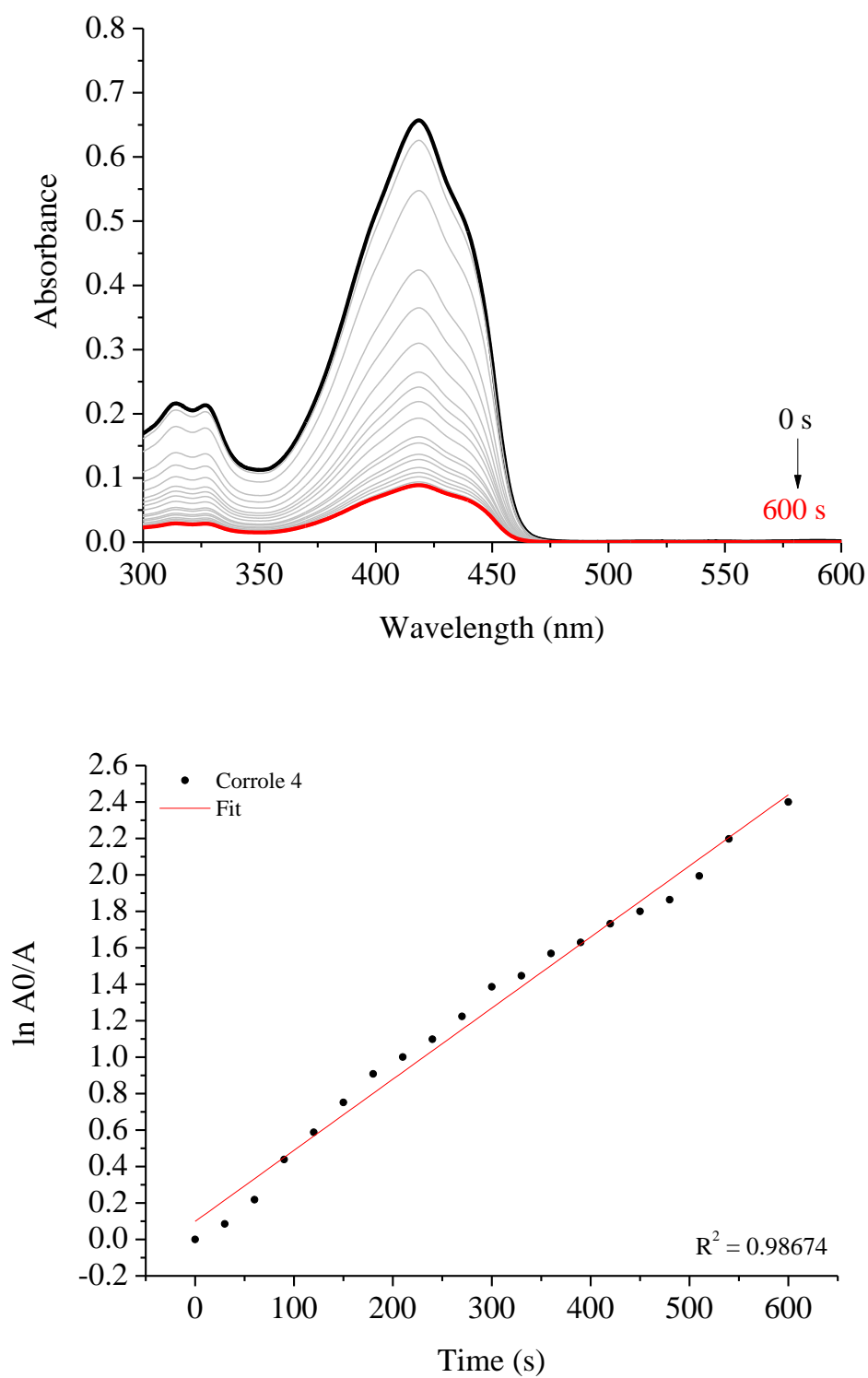


**Figure S51.** (up) DPBF photo-oxidation assay of corrole **2** in DMSO solution, by red-light irradiation source at 600 s and (down)  $\ln A_0/A$  versus time plot.

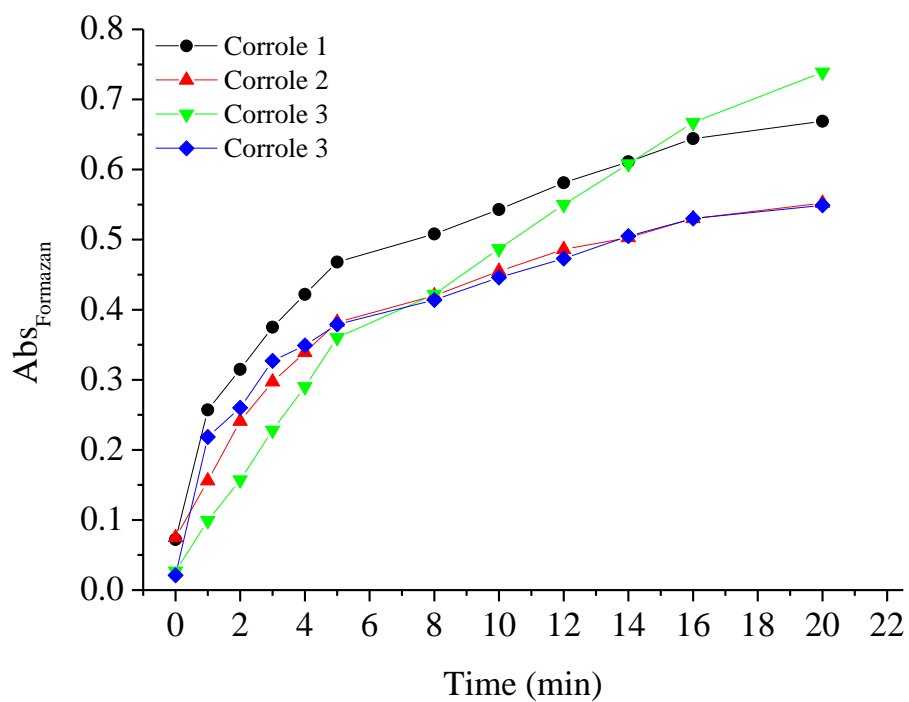


**Figure S52.** (up) DPBF photo-oxidation assay of corrole **3** in DMSO solution, by red-light irradiation source at 600 s and (down)  $\ln A_0/A$  versus time plot.

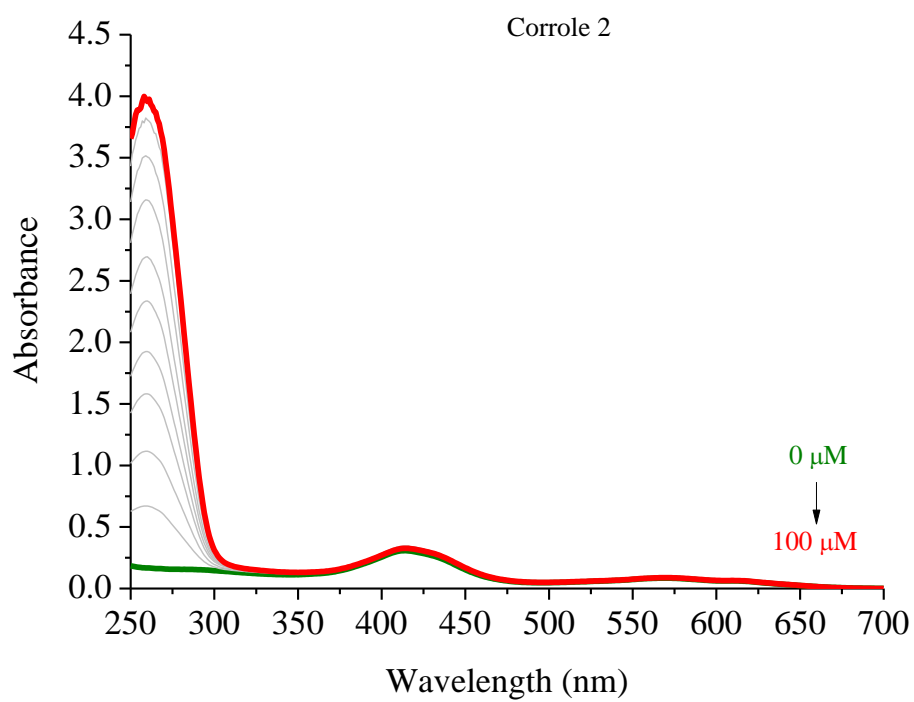


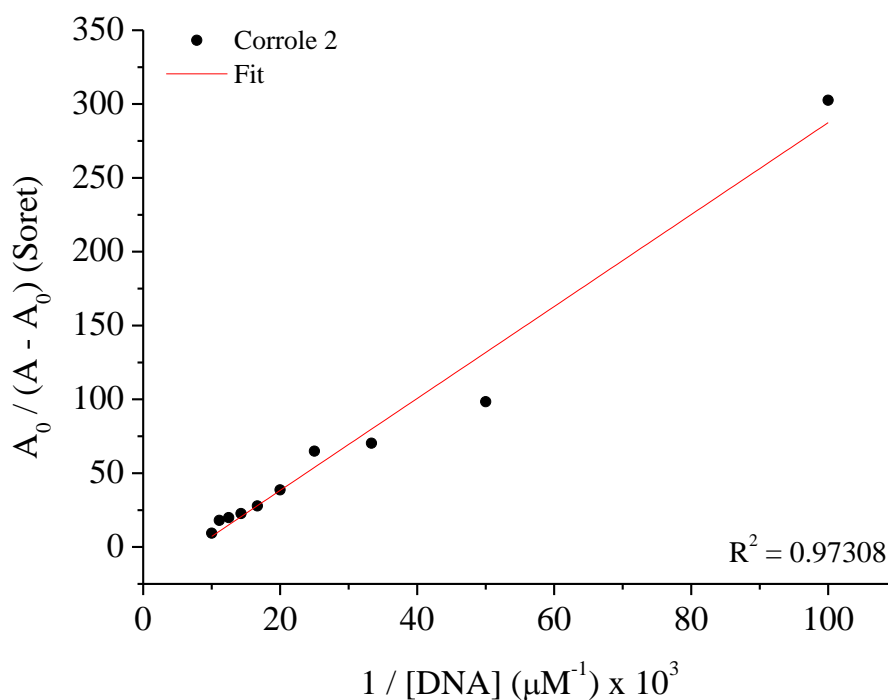


**Figure S53.** (up) DPBF photo-oxidation assay of corrole 4 in DMSO solution, by red-light irradiation source at 600 s and (down)  $\ln A_0/A$  versus time plot.

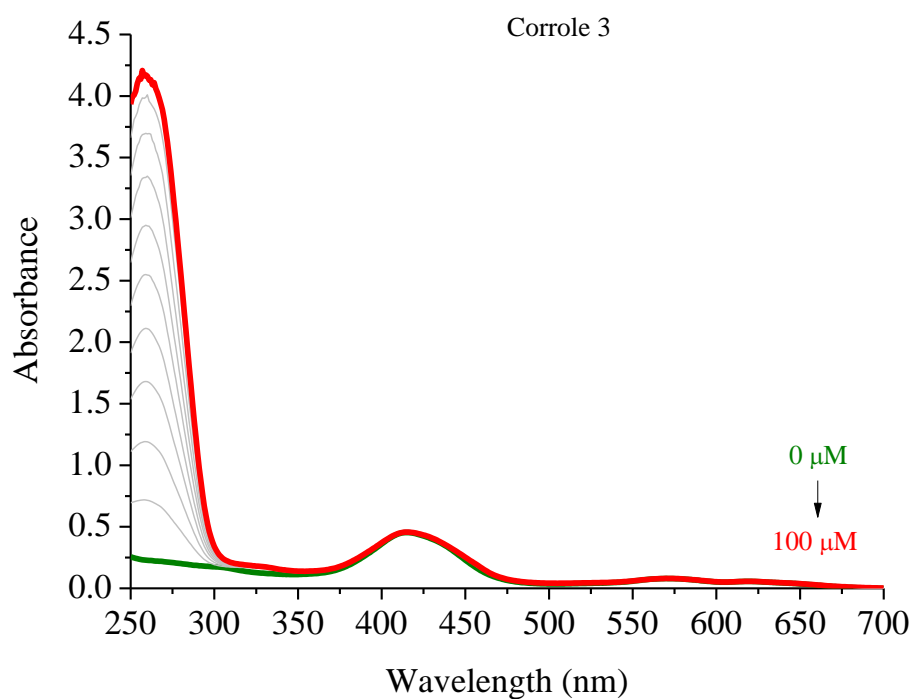


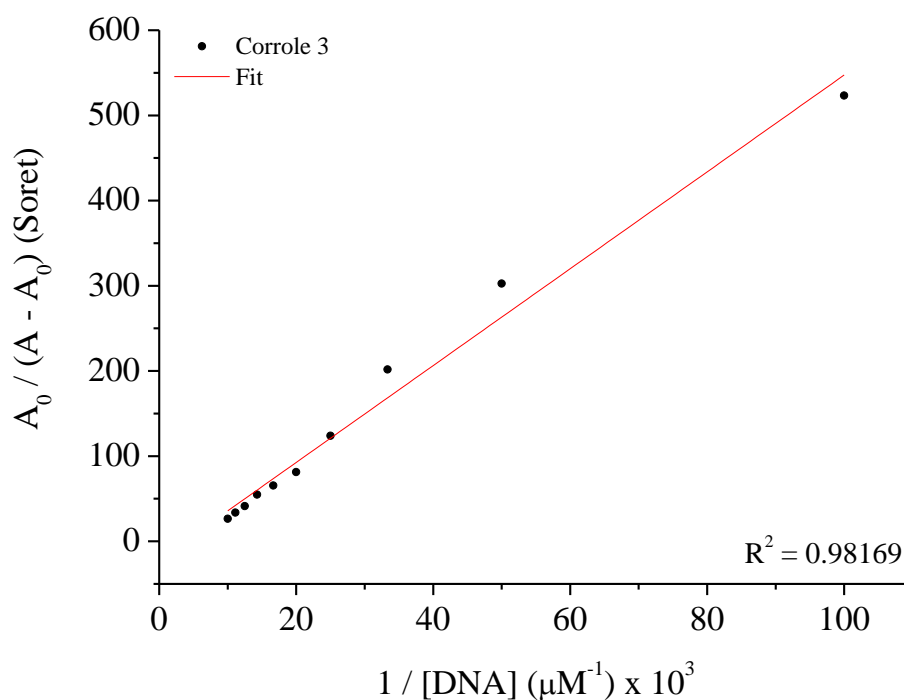
**Figure S54.** NBT reduction assay of corroles **1-4** in DMSO solution, by white-light irradiation source at 20 min.



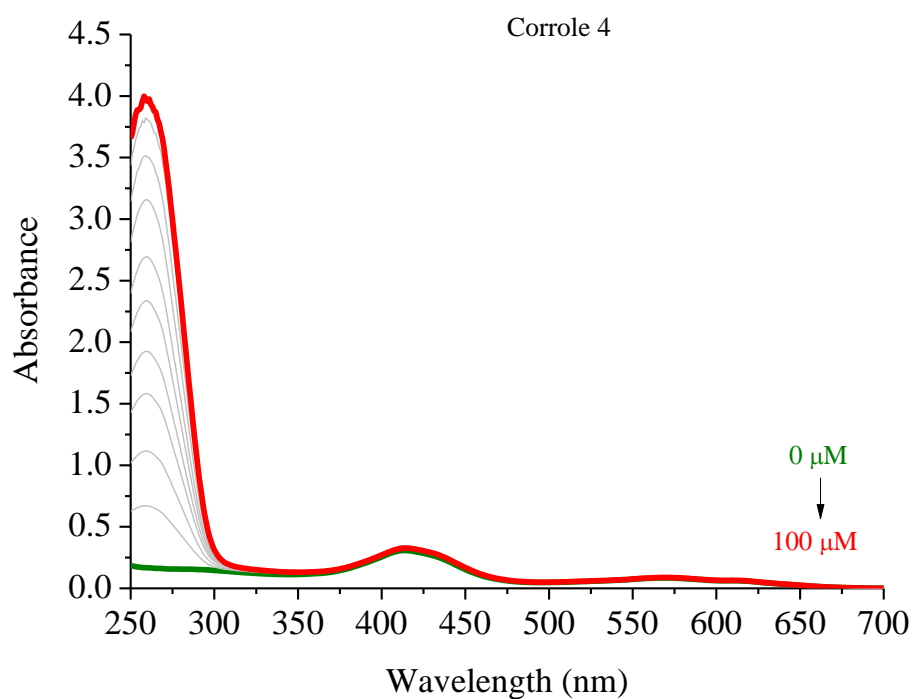


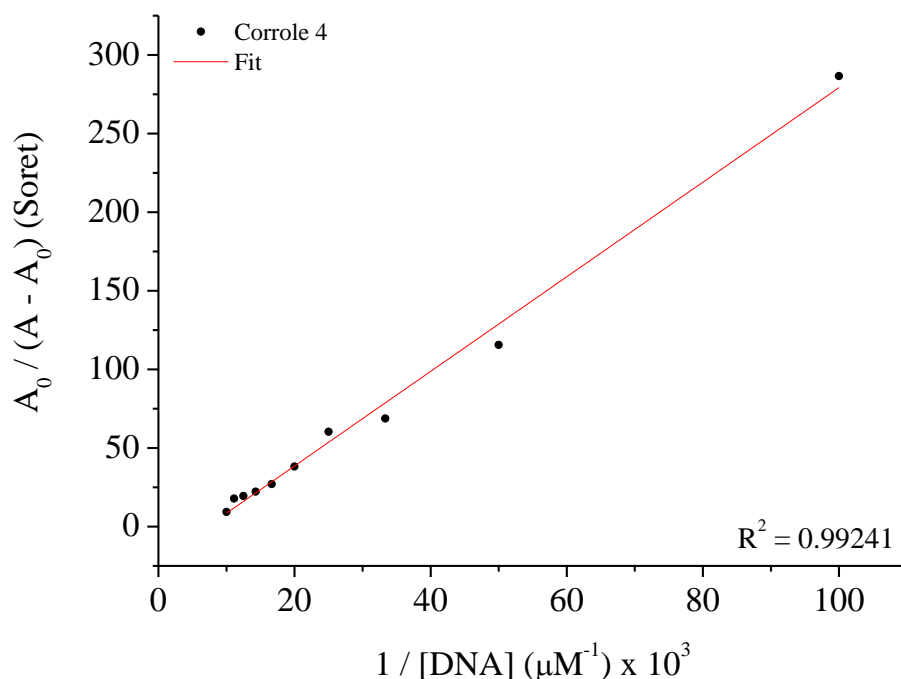
**Figure S55.** (up) UV-Vis spectra of the corrole **2** upon successive additions of CT-DNA concentrations (0 to 100  $\mu\text{M}$ ) in DMSO(5%)/Tris-HCl pH 7.4 mixture buffered solution. (down) Benesi-Hildebrandt plots of  $A_0 / (A - A_0)$  versus  $1 / [\text{CT-DNA}]$ .



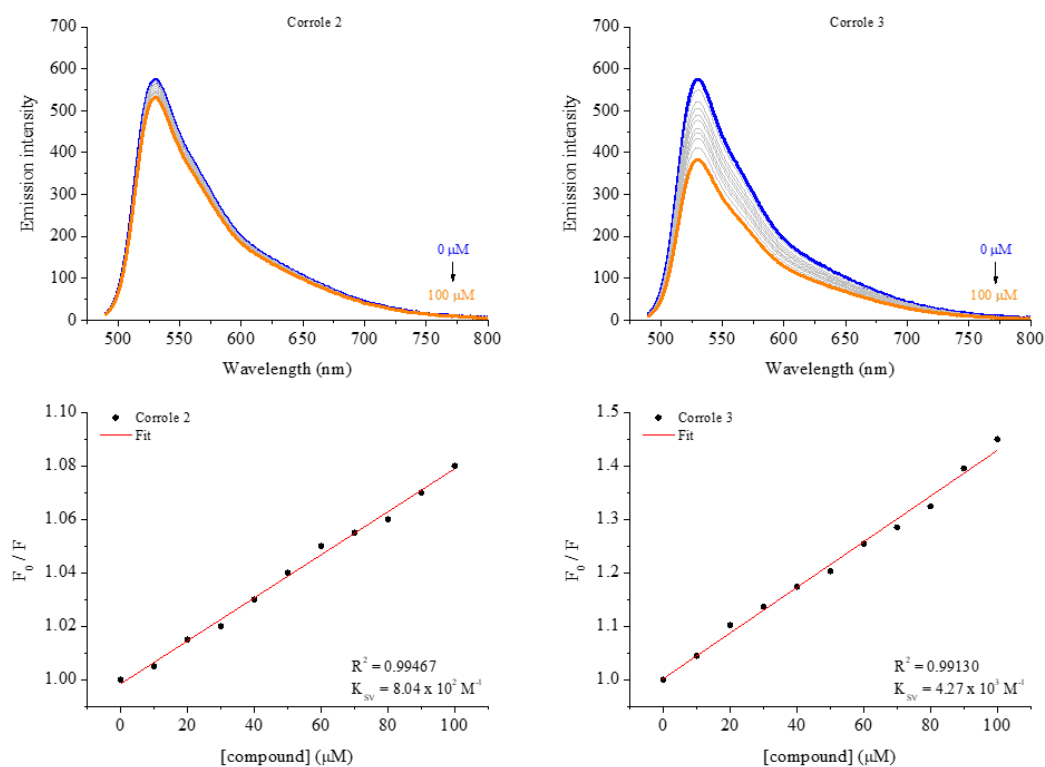


**Figure S56.** (up) UV-Vis spectra of the corrole **3** upon successive additions of CT-DNA concentrations (0 to 100  $\mu\text{M}$ ) in DMSO(5%)/Tris-HCl pH 7.4 mixture buffered solution. (down) Benesi-Hildebrandt plots of  $A_0 / (A - A_0)$  versus  $1 / [\text{CT-DNA}]$ .

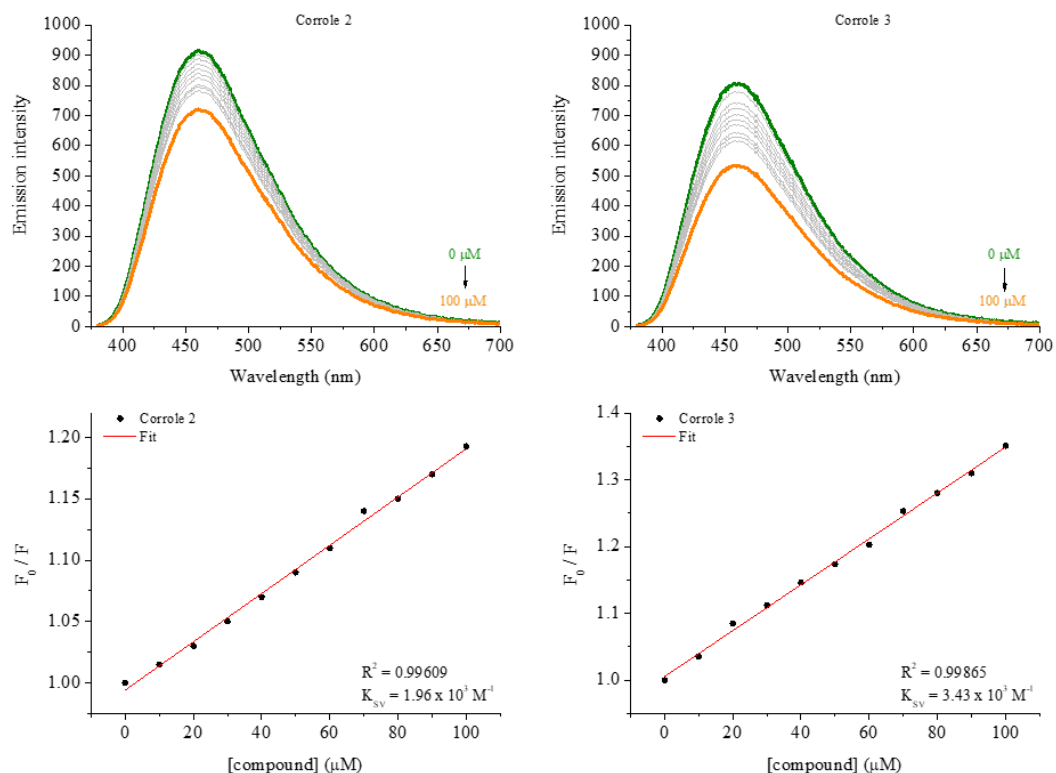




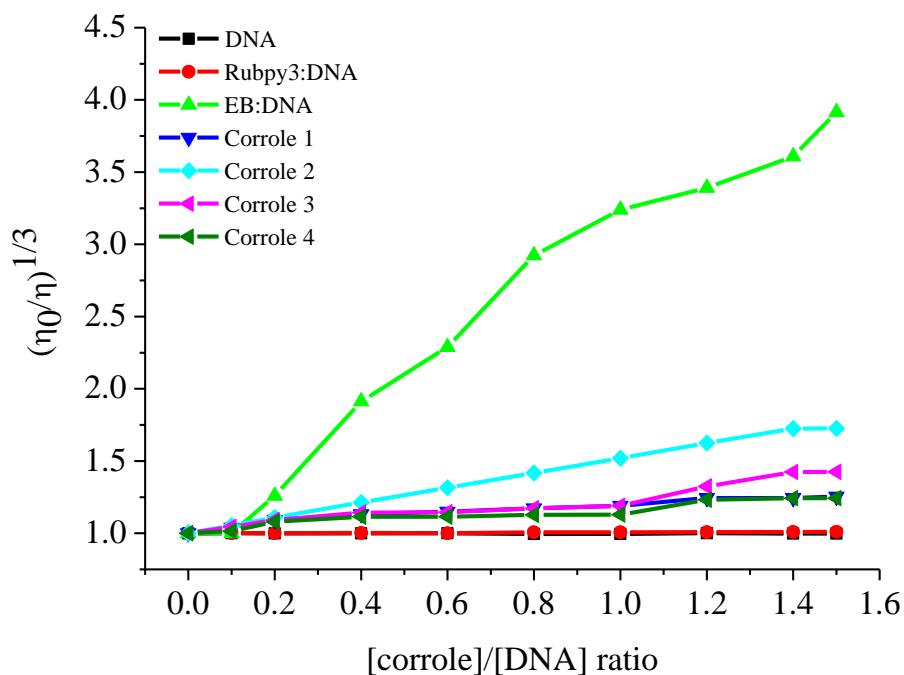
**Figure S57.** (up) UV-Vis spectra of the corrole **4** upon successive additions of CT-DNA concentrations (0 to 100  $\mu\text{M}$ ) in DMSO(5%)/Tris-HCl pH 7.4 mixture buffered solution. (down) Benesi-Hildebrandt plots of  $A_0 / (A - A_0)$  versus  $1 / [\text{CT-DNA}]$ .



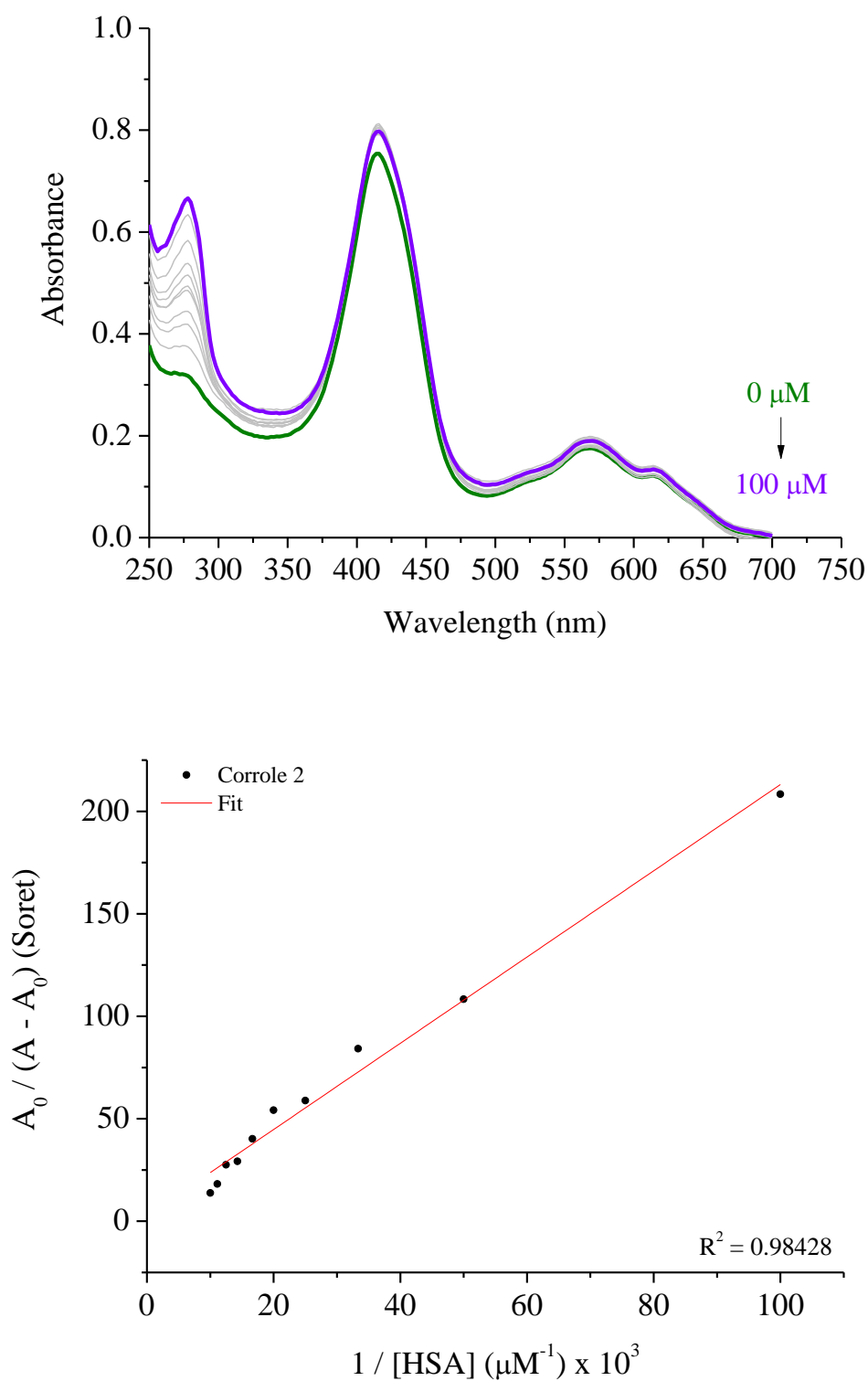
**Figure S58.** Steady-state fluorescence emission spectra for AO:DNA without and in the presence of corroles **2** and **3**, in DMSO(5%)/Tris-HCl pH 7.4 mixture buffered solution. Graphs shows the plot  $F_0 / F$  versus [corrole]. [corrole] = 0–100  $\mu\text{M}$ .



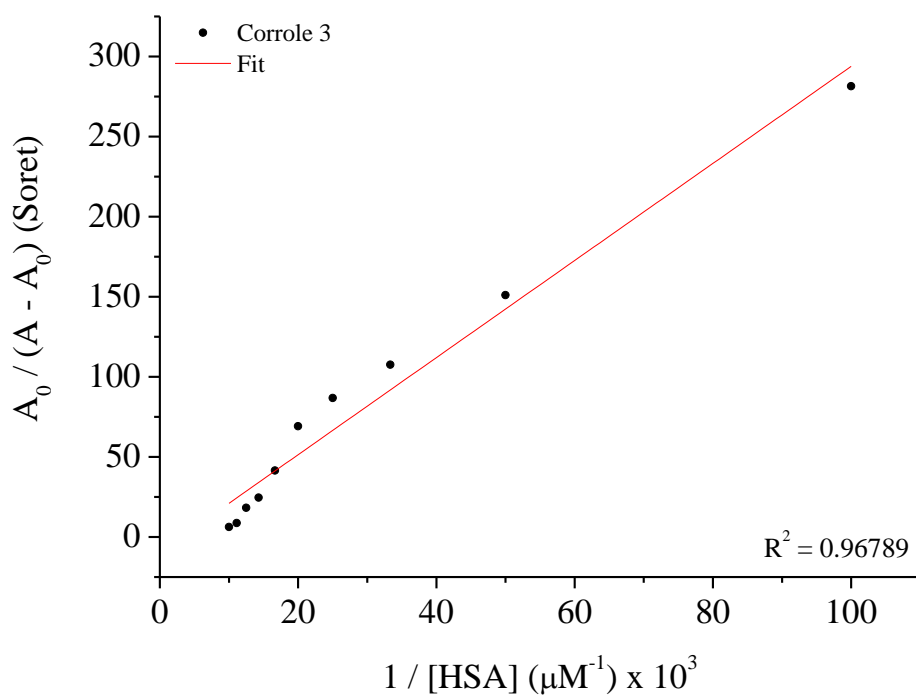
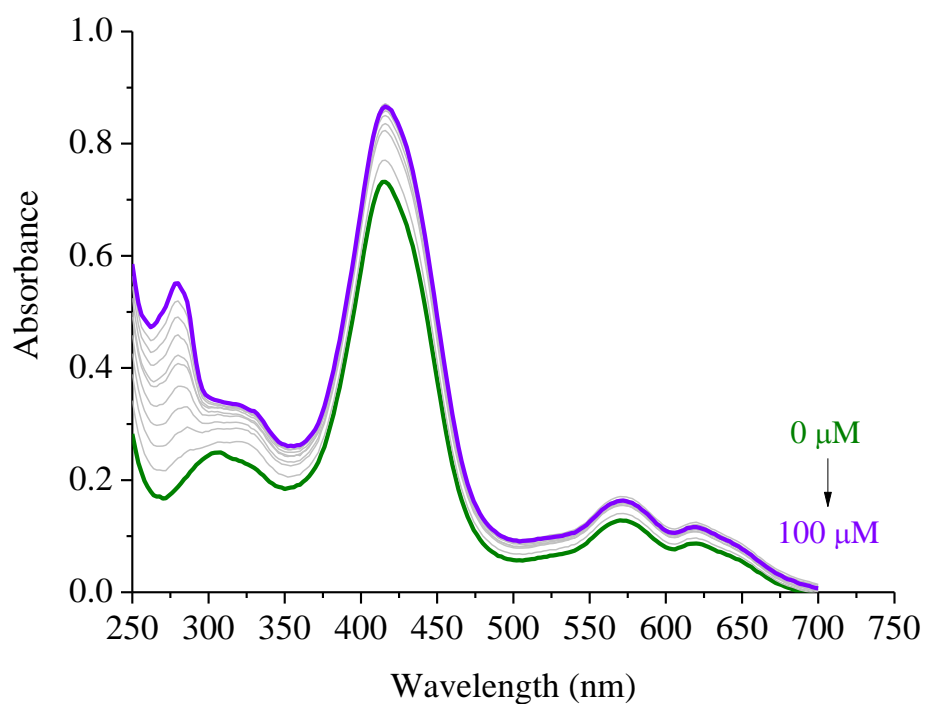
**Figure S59.** Steady-state fluorescence emission spectra for DAPI:DNA without and in the presence of corroles **2** and **3**, in DMSO(5%)/Tris-HCl pH 7.4 mixture buffered solution. Graphs shows the plot  $F_0/F$  versus [corrole]. [corrole] = 0–100  $\mu\text{M}$ .



**Figure S60.** Viscosimetry assay of CT-DNA without and in the presence of corroles **1-4**, in DMSO(5%)/Tris-HCl pH 7.4 mixture buffered solution.

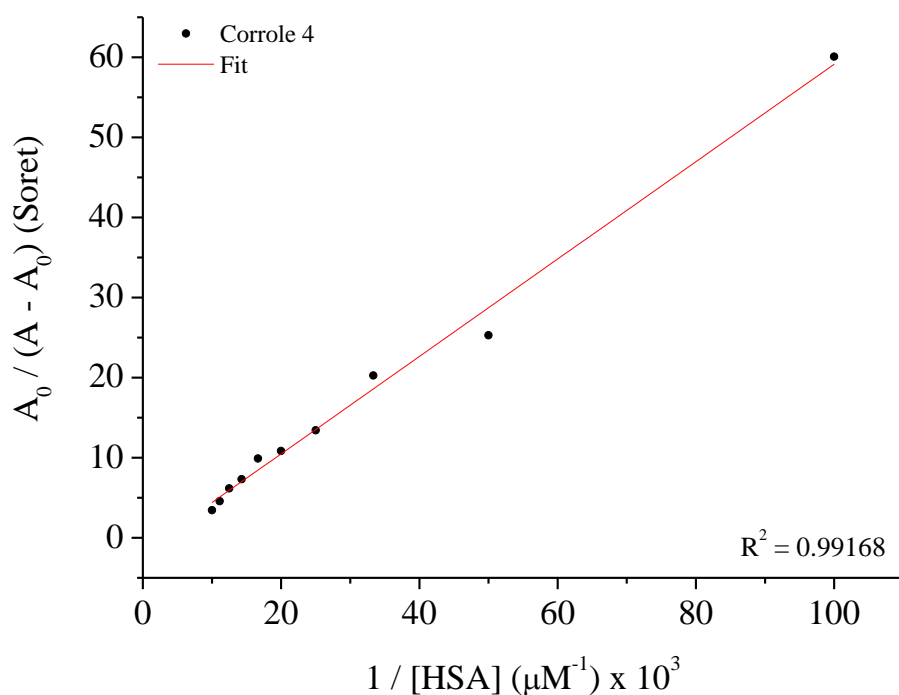
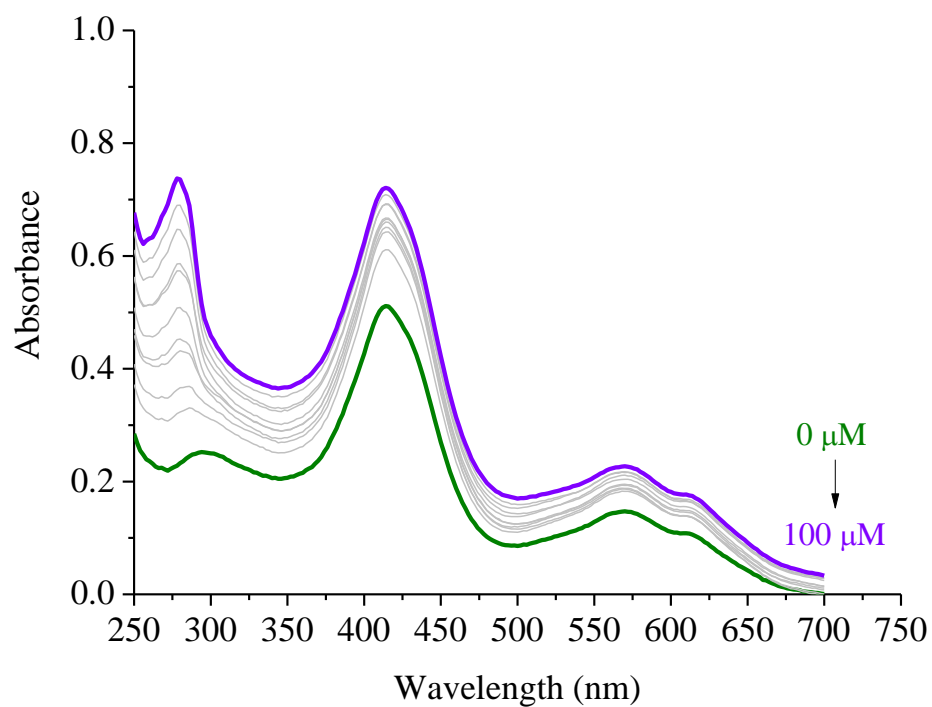


**Figure S61.** (up) UV-Vis spectra of the corrole 2 upon successive additions of HSA concentrations (0 to 100  $\mu\text{M}$ ) in DMSO(5%)/Tris-HCl pH 7.4 mixture buffered solution. (down) Benesi-Hildebrandt plots of  $A_0 / (A - A_0)$  versus  $1 / [\text{HSA}]$ .

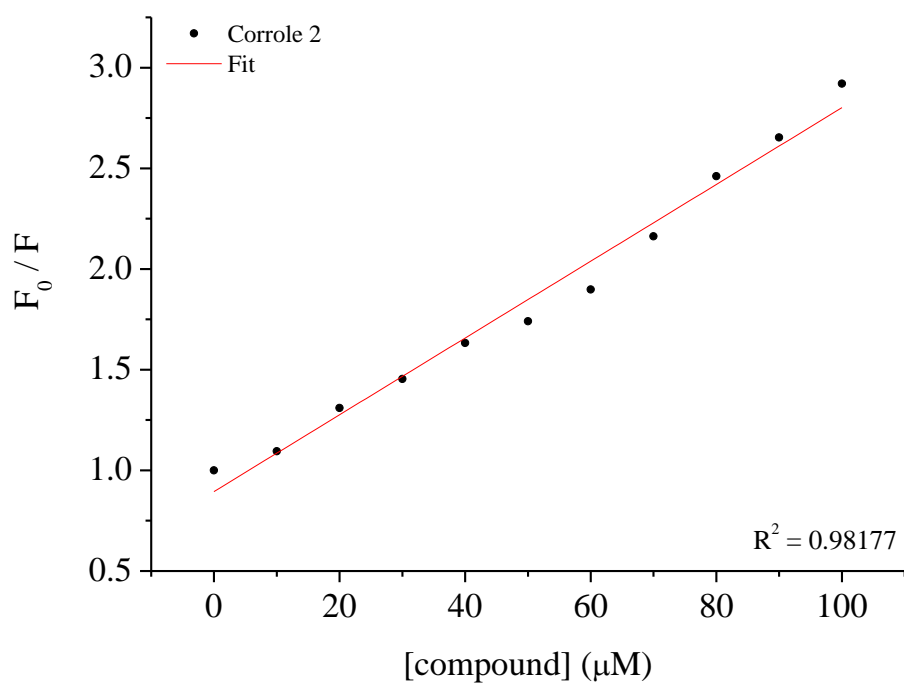
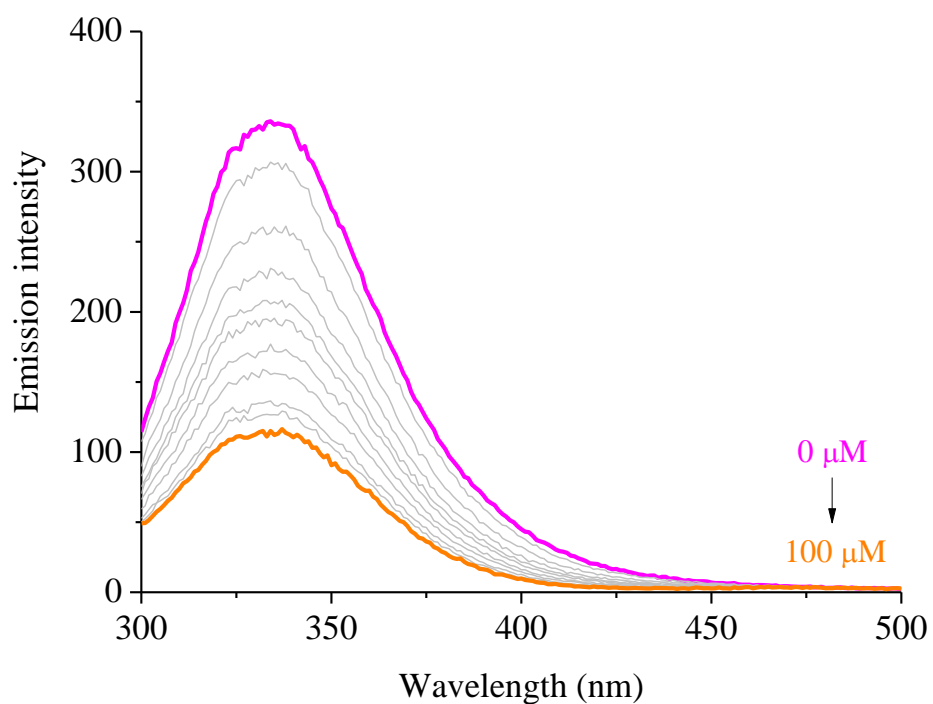


**Figure S62.** (up) UV-Vis spectra of the corrole **3** upon successive additions of HSA concentrations (0 to 100  $\mu\text{M}$ ) in DMSO(5%)/Tris-HCl pH 7.4 mixture buffered solution. (down) Benesi-Hidelbrandt plots of  $A_0 / (A - A_0)$  versus  $1 / [\text{HSA}]$ .

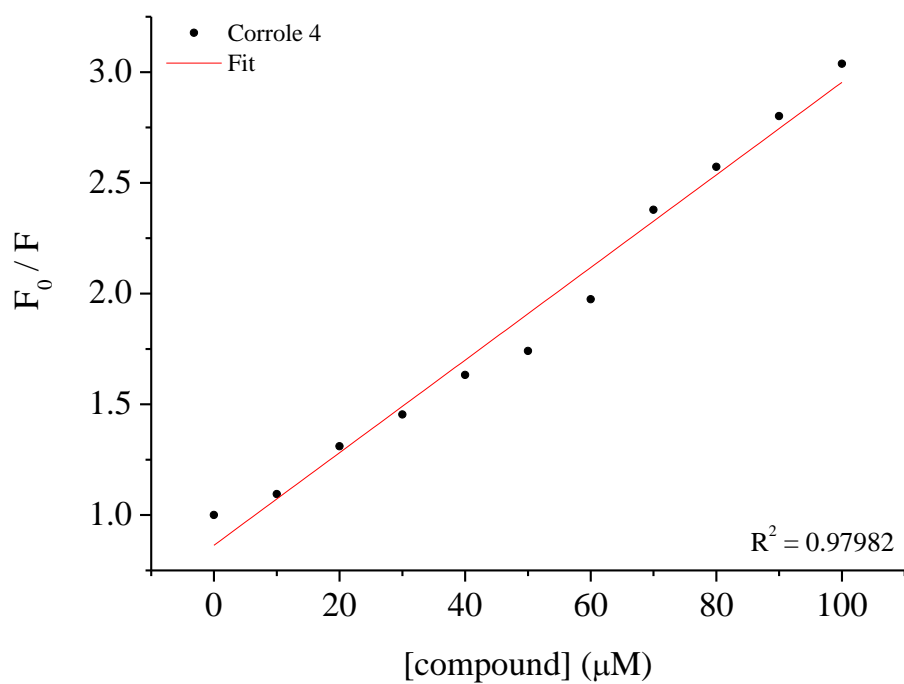
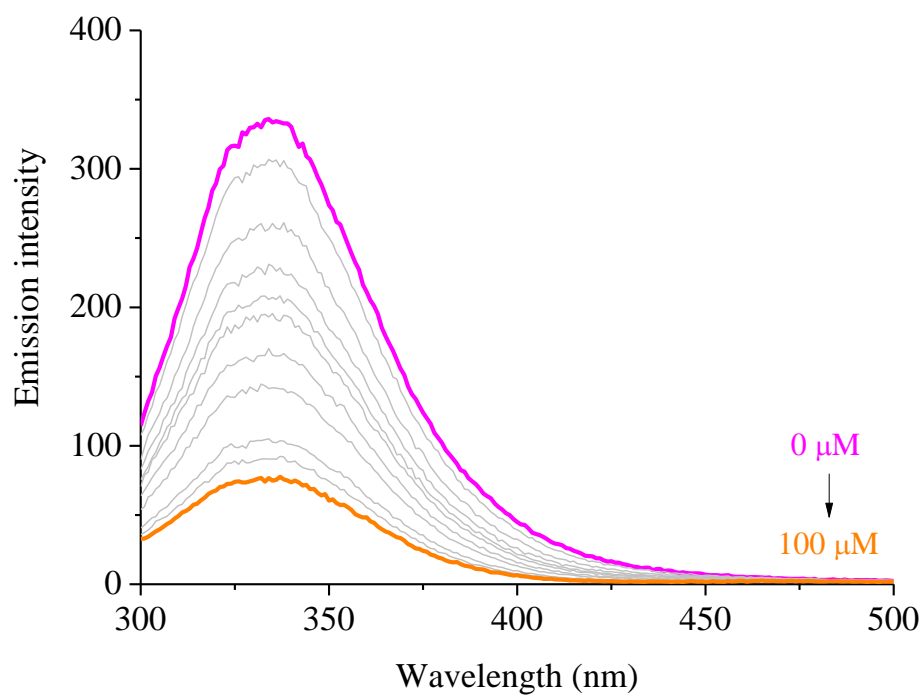




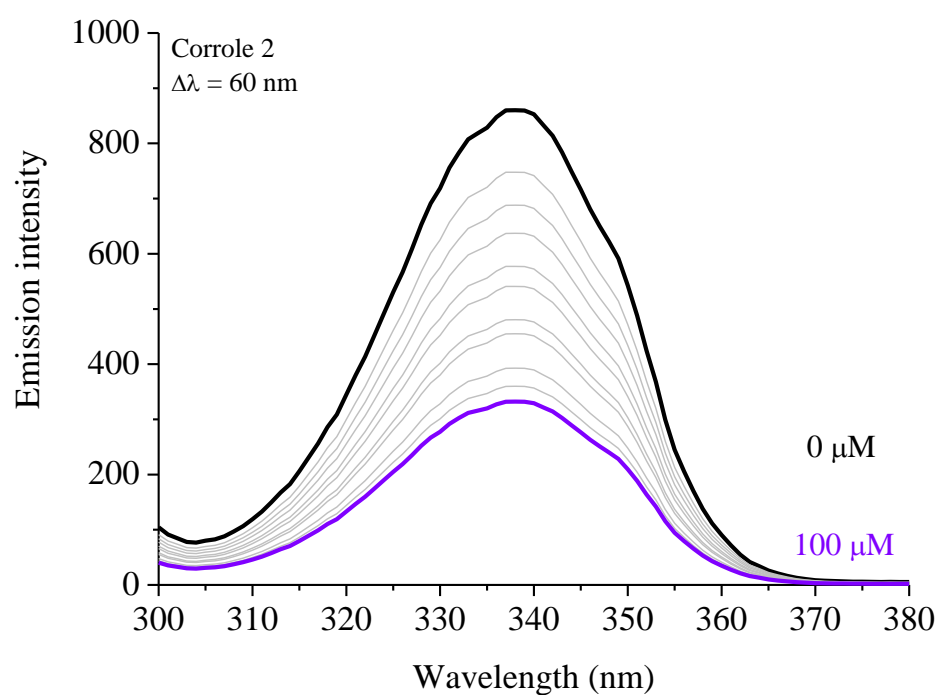
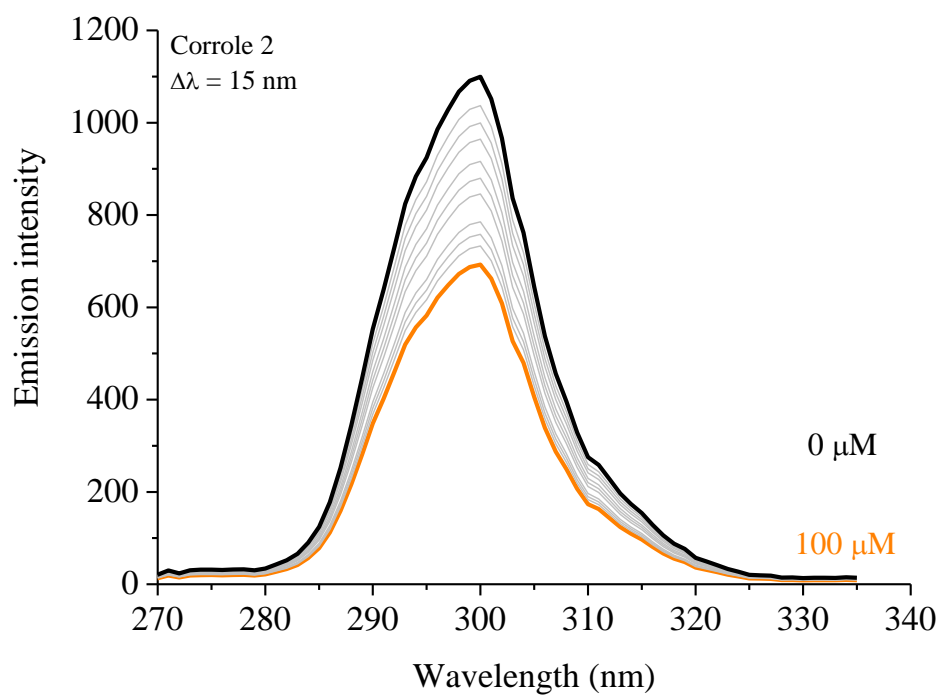
**Figure S63.** **(up)** UV-Vis spectra of the corrole **4** upon successive additions of HSA concentrations (0 to 100  $\mu\text{M}$ ) in DMSO(5%)/Tris-HCl pH 7.4 mixture buffered solution. **(down)** Benesi-Hidelandt plots of  $A_0 / (A - A_0)$  versus  $1 / [\text{HSA}]$ .



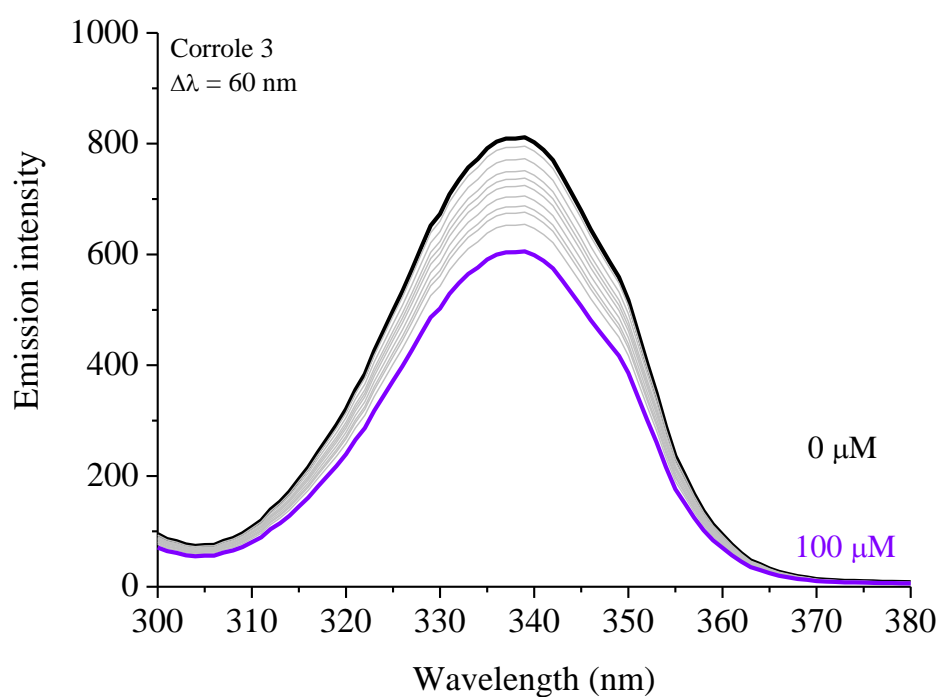
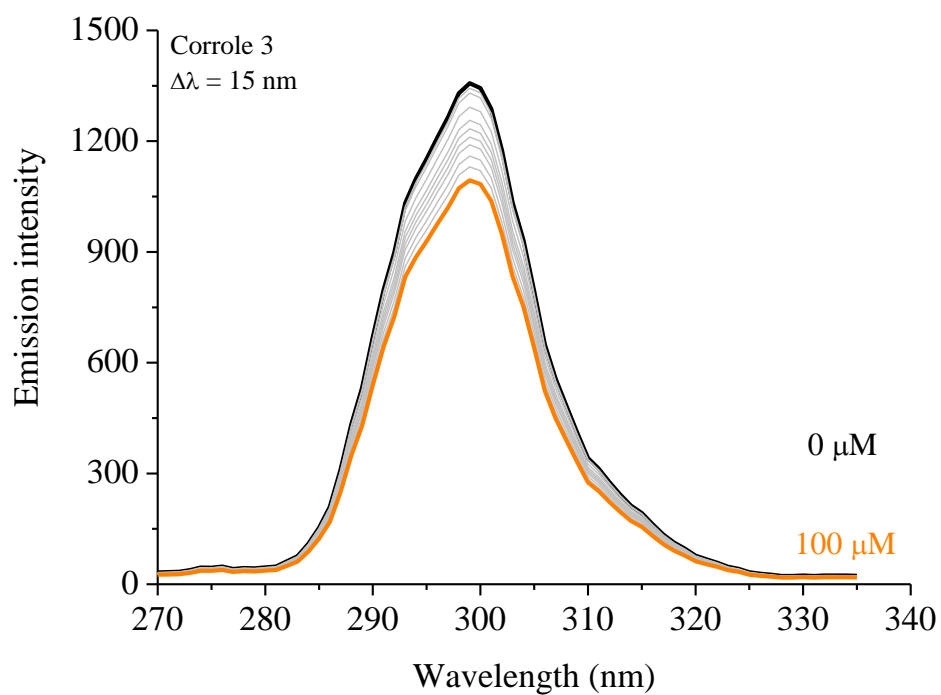
**Figure S64.** Steady-state fluorescence emission spectra for HSA without and in the presence of corrole 2, in in DMSO(5%)/Tris-HCl pH 7.4 mixture buffered solution. Graph shows the plot  $F_0/F$  versus [corrole]. [corrole] = 0–100  $\mu\text{M}$ .



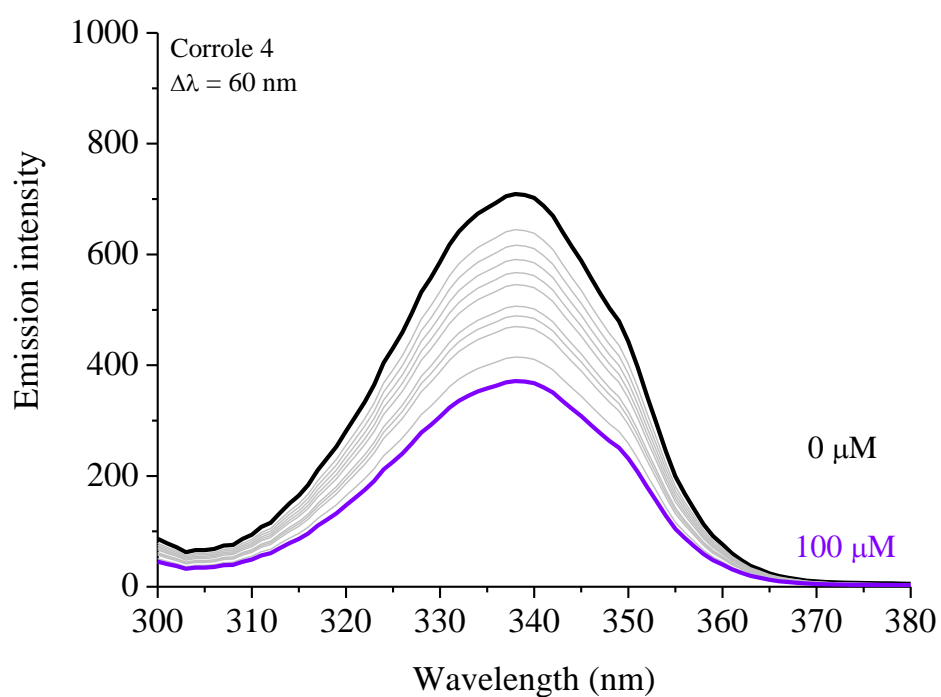
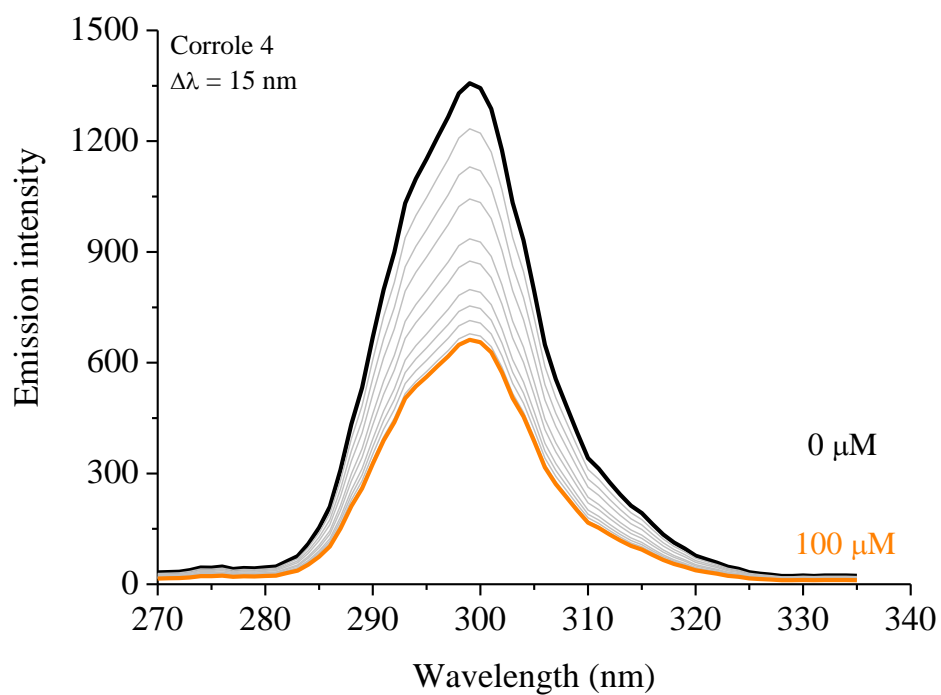
**Figure S65.** Steady-state fluorescence emission spectra for HSA without and in the presence of corrole 4, in in DMSO(5%)/Tris-HCl pH 7.4 mixture buffered solution. Graph shows the plot  $F_0/F$  versus [corrole]. [corrole] = 0–100  $\mu\text{M}$ .



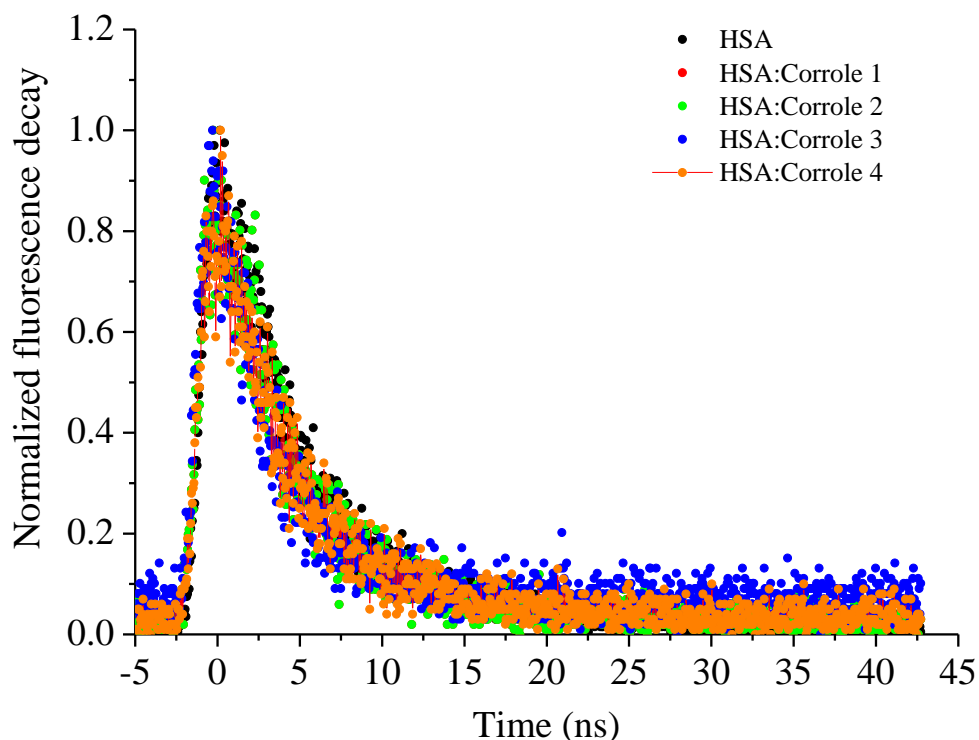
**Figure S66.** SF fluorescence emission spectra for HSA without and in the presence of corrole 2, in DMSO(5%)/Tris-HCl pH 7.4 mixture buffered solution, when (up)  $\Delta\lambda = 15 \text{ nm}$  and (down)  $\Delta\lambda = 60 \text{ nm}$ .



**Figure S67.** SF fluorescence emission spectra for HSA without and in the presence of corrole **3**, in DMSO(5%)/Tris-HCl pH 7.4 mixture buffered solution, when (up)  $\Delta\lambda = 15 \text{ nm}$  and (down)  $\Delta\lambda = 60 \text{ nm}$ .



**Figure S68.** SF fluorescence emission spectra for HSA without and in the presence of corrole 4, in DMSO(5%)/Tris-HCl pH 7.4 mixture buffered solution, when (up)  $\Delta\lambda = 15 \text{ nm}$  and (down)  $\Delta\lambda = 60 \text{ nm}$ .



**Figure S69.** Normalized fluorescence decays of HSA in DMSO(5%)/Tris-HCl pH 7.4 mixture buffered solution, in the absence or in the presence of corroles **1-4**.

**Table S1.** The absorption wavelengths,  $\lambda$  (nm), and the oscillator strengths,  $f$ , of the two main peaks of the Soret and Q-bands of the tautomeric state T1, in DMSO solvent, for the studied corrole compounds.

	Soret				Q			
	$\lambda$ (nm)	$f$	$\lambda$ (nm)	$f$	$\lambda$ (nm)	$f$	$\lambda$ (nm)	$f$
Corrole 1	357.36	1.4144	373.24	1.3183	544.99	0.1032	562.68	0.2926
Corrole 2	358.76	1.4011	375.81	1.3708	547.06	0.1053	564.06	0.2893
Corrole 3	360.69	1.3770	381.29	1.4022	554.05	0.0842	575.62	0.3195
Corrole 4	361.38	1.3800	382.45	1.5170	552.76	0.0793	573.38	0.3105

**Table S2.** The absorption wavelengths,  $\lambda$  (nm), and the oscillator strengths,  $f$ , of the two main peaks of the Soret and Q-bands of the tautomeric state T2, in DMSO solvent, for the studied corrole compounds.

	Soret				Q			
	$\lambda$ (nm)	$f$	$\lambda$ (nm)	$f$	$\lambda$ (nm)	$f$	$\lambda$ (nm)	$f$
Corrole 1	366.45	1.4491	381.47	1.4273	533.03	0.0356	581.29	0.1634
Corrole 2	368.48	1.4580	386.81	1.4265	538.55	0.0527	588.15	0.1885
Corrole 3	370.57	1.4518	390.31	1.4458	543.60	0.0376	596.63	0.2187
Corrole 4	371.36	1.4600	391.58	1.5509	542.74	0.0356	595.04	0.2077

**Table S3.** Fluorescence decay data of HSA in the absence or in the presence of corroles **1-4**.

Corrole	tf (ns)	$\chi^2$
HSA:1	$4.89 \pm 0.002$	1.03680
HSA:2	$4.77 \pm 0.002$	1.17756
HSA:3	$4.60 \pm 0.002$	0.95752
HSA:4	$4.60 \pm 0.002$	1.07678
HSA	$5.25 \pm 0.001$	1.13768

**Table S4.** Molecular docking results for the interaction between DNA:corroles in the minor groove.

Corrole	Nitrogenated bases	Interaction	Distance (Å)
<b>Corrole 2</b>	DG-04	Van der Waals	1.50
	DA-05	Van der Waals	2.30
	DT-20	Van der Waals	3.70
	DC-21	Van der Waals	3.40
	DG-22	Hydrogen bonding	3.20
<b>Corrole 3</b>	DG-04	Van der Waals	2.80
	DA-05	Van der Waals	1.70
	DA-06	Hydrogen bonding	1.90
	DT-20	Hydrogen bonding	3.10
	DC-21	Van der Waals	2.00
	DG-22	Hydrogen bonding	3.20
<b>Corrole 4</b>	DG-02	Hydrogen bonding	3.60
	DC-23	Van der Waals	3.40
	DG-22	Van der Waals	2.80
	DG-04	Van der Waals	1.40
	DC-21	Van der Waals	3.80
	DA-05	Van der Waals	2.40
	DT-20	Van der Waals	3.30

**Table S5.** Molecular docking results for the interaction between HSA:corroles for the corresponding main binding site.

Corrole	Amino acid residue	Interaction	Distance (Å)
<b>Corrole 2</b>	Lys-195	Hydrogen bonding	2.90
	Lys-199	Van der Waals	1.50
	Trp-214	Van der Waals	2.80
	Arg-222	Hydrogen bonding	3.00
	His-242	Van der Waals	3.10
	Cys-245	Van der Waals	2.80
	Arg-257	Hydrogen bonding	3.70
	Ala-291	Van der Waals	3.40
	Glu-292	Van der Waals	2.20
	Val-343	Van der Waals	2.40



	Arg-114	Hydrogen bonding	3.70
	Leu-115	Van der Waals	3.60
	Arg-117	Van der Waals	1.40
<b>Corrole 3</b>	Ile-142	Van der Waals	1.50
<b>Corrole 4</b>	His-146	Van der Waals	3.40
	Tyr-161	Hydrogen bonding	2.60
	Leu-182	Van der Waals	2.40
	Arg-186	Van der Waals	3.20
	Lys-190	Van der Waals	2.70